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UNITED STATES DEPARTMENT OF AGRICULTURE

DEPARTMENT BULLETIN No. 1179

Washington, D. C. ▼ December, 1923

INVESTIGATIONS OF THE MANUFACTURE OF PHOSPHORIC ACID BY THE VOLATILIZATION PROCESS

By

WILLIAM H. WAGGAMAN, Scientist in Investigation of Fertilizer Resources; HENRY W. EASTERWOOD, Chemist, and THOMAS B. TURLEY, Operation Engineer, Investigation of Fertilizer Resources, Bureau of Soils

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WASHINGTON
GOVERNMENT PRINTING OFFICE
1923

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By WILLIAM H. WAGGAMAN, *Scientist in Investigation of Fertilizer Resources;* HENRY W. EASTERWOOD, *Chemist,* and THOMAS B. TURLEY, *Operation Engineer, Investigation of Fertilizer Resources, Bureau of Soils.*

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INTRODUCTION.

During the last decade there has been a distinct tendency toward higher specialization in American industries. The late war, with its demands for a greater output of practically all agricultural and manufactured products, further stimulated industrial effort, and now the high cost of labor, increased freight rates, and the keen competition which has grown out of the postwar period has forced upon us the necessity of even greater efficiency in our industrial processes.

While the American fertilizer industry up to the time of the European war had shown a rather steady, healthy growth, in some regards it had lagged considerably. This was due in part, no doubt, to the fact that it had always been an industry utilizing refuse and waste products generally regarded as unfit for other purposes, and partly to the fact that the American farmer had grown so accustomed to the use of relatively low analysis fertilizers that it was

[1] For complete treatise on the mining of phosphate rock and various methods of manufacturing phosphoric acid and phosphates for fertilizer and other purposes the reader is referred to a book entitled "Phosphoric Acid, Phosphates, and Phosphatic Fertilizers," by Wm. H. Waggaman and Henry W. Easterwood, which will appear shortly as a monograph of the American Chemical Society.

difficult for him to see that the same fertilizer value might be carried in very much smaller bulk, and that by using the more concentrated materials he could actually obtain the unit of plant food at a considerably lower cost, owing to the saving effected in storage, shipping, and handling charges.

The gradual realization, however, that many of these low analysis materials, such as tankage, cottonseed meal, fish scrap, and the like, could be used much more profitably as stock feed than as fertilizer resulted in the manufacturers turning toward the higher grade materials and chemical compounds carrying nitrogen, phosphoric acid, and potash to make up the deficit caused by the withdrawal of the organic ammoniates for the feeding of animals. Many of the high-grade materials and chemical products useful in the manufacture of fertilizers are also essential in the production of munitions, and therefore this double demand during the war period probably did more than anything else toward initiating researches which will eventually establish the fertilizer industry on a sound chemical basis.[2] Of the three main fertilizing ingredients, potash, nitrogen, and phosphoric acid, the last mentioned is by far the most extensively used in American agriculture, and therefore the production of phosphates and fertilizers carrying phosphoric acid have received more attention than any other. It is true that an American potash industry was built up during the war, where none existed before, but our output of this fertilizer ingredient has now been very much curtailed by foreign competition[3] and unless we can perfect methods of recovering potash as a by-product of other industries the economic production of this material from American sources appears doubtful.

The researches on methods of fixing atmospheric nitrogen which are being carried on in this department and the probable development of much cheaper hydroelectric power than is at present available will eventually establish large industries wherein synthetic nitrogen compounds will be manufactured as main products, but at present the mining and manufacturing of phosphates for agricultural purposes is the only branch of our immense fertilizer industry in which we are not dependent either upon foreign sources or upon the by-products of other industries for the necessary supply of raw materials.

In recent years pyrolytic methods of producing phosphoric acid have been receiving a great deal of consideration, and rather exhaustive investigations have been conducted in this bureau with a view to establishing their commercial possibilities. From the data obtained and the progress so far made on this problem both in the bureau and by outside commercial interests it seems highly probable that this process will be employed in the near future to supplement, in part at least, the now almost universally applied method of making water-soluble phosphates by treating phosphate rock with sulphuric acid.

PRINCIPLES INVOLVED IN THE VOLATILIZATION PROCESS.

While the volatilization process for producing phosphoric acid has only recently assumed much prominence, the general scheme employed is by no means a new one, it being based on the old method so long in use for the manufacture of elementary phosphorus.

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[2] Whitney, Milton. The Fertilizer Situation. Chem. and Met. Eng. 22, p. 1021 (1920).
[3] Nourse, M. R. Potash in 1921. In Mineral Resources, U. S. Geological Survey, part 2, pp. 51–63 (1922).

The fundamental principle involved is that at high temperatures (1,600° to 1,800° C.) silica assumes the properties of a relatively strong acid in so far as its ability to combine with bases is concerned, and therefore it can displace the phosphoric acid of phosphate rock forming silicates of lime and free phosphoric anhydride (P_2O_5). The latter compound being highly volatile at elevated temperatures is driven off as a fume and may be collected either by absorption in water or by means of the Cottrell electrical precipitator, which is described later in this bulletin. When carbon or coke is added to the mixture to be smelted elemental phosphorus is produced, and if reducing conditions are maintained throughout the operation the decomposition of the rock and expulsion of its phosphorus content may be brought about at considerably lower temperatures (1,300° to 1,500° C.).

According to Nielsen,[4] while tricalcium phosphate and silica begin to react at a temperature of 1,150° C. and continue to form various compounds up to 1,650° C., unless a reducing agent is present these chemical changes merely consist in certain combinations of the two substances and no phosphoric acid is evolved. This same author states that while CO will not reduce tricalcium phosphate this latter compound is completely reducible by carbon, the reduction beginning at 1,400° C. He claims, however, that there always remains some phosphorus in the residue because the CaO formed unites with the undecomposed calcium phosphate to form more basic compounds of phosphoric acid which are not reduced by carbon. Peacock[5] takes issue with Nielsen on this point, stating that if the evolved gases are removed as fast as they are formed complete dispersion of phosphorus is obtained by heating mixtures of phosphate rock and carbon. Carnot,[6] Stead,[7] and Kroll,[8] however, have recognized the existence of certain nonvolatile compounds of phosphoric acid, silica, and lime in basic slag where an excess of lime is always present, and it seems logical to the writers that such compounds would form in simple mixtures of phosphate rock and carbon after sufficient P_2O_5 were evolved to render the residue basic. Nielson is wrong, however, in his conclusion that P_2O_5 is not evolved upon heating mixtures of phosphate rock and silica in the absence of a reducing agent, for later experimentation has shown that where a relatively high percentage of silica is added phosphoric acid is copiously evolved when the temperature of the mass approaches 1,800° C.

The presence of a reducing agent is essential, however, in order to bring about the volatilization of phosphoric acid (or phosphorus) at the lower temperatures and the writers have found that by briquetting finely ground mixtures of phosphate rock, silica, and coke (thus insuring reducing conditions within the mass and a close contact between the reacting materials) the volatilization of P_2O_5 begins considerably below 1,300° C. and by prolonged heating at this temperature the bulk of this acid may be driven off.

While various silicates of lime are no doubt formed in smelting mixtures of phosphate rock, sand, and coke, depending on the silica-

[4] Ferrum, vol. 10, p. 97-111 (1913). Translated in American Fertilizer, vol. 39, No. 6, p. 63 (1913).
[5] American Fertilizer, vol. 39, No. 6, p. 67 (1913).
[6] Compt. Rend. 97, p. 136 (1883).
[7] Trans. Chem. Soc. 51, p. 601 (1887).
[8] Jour. Iron and Steel Inst. 2, p. 126 (1911).

lime ratio in the charge, the general course of the reaction is usually represented by the following simple equation:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C = 3CaSiO_3 + P_2 + 5CO.$$

The phosphorus evolved is oxidized by air or carbon dioxide to phosphorus pentoxide either within or outside of the furnace proper according to the following equation:

$$(1) \quad 2P_2 + 5O_2 = 2P_2O_5$$
$$(2) \quad P_2 + 5CO_2 = P_2O_5 + 5CO.$$

Actual experience has proven, however, that in oxidizing phosphorus either with air or carbon dioxide there is ordinarily sufficient moisture present to form orthophosphoric acid and even where the Cottrell method of precipitation is employed the final product is a liquid. This reaction is represented thus:

$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

ADVANTAGES OF THE VOLATILIZATION PROCESS.

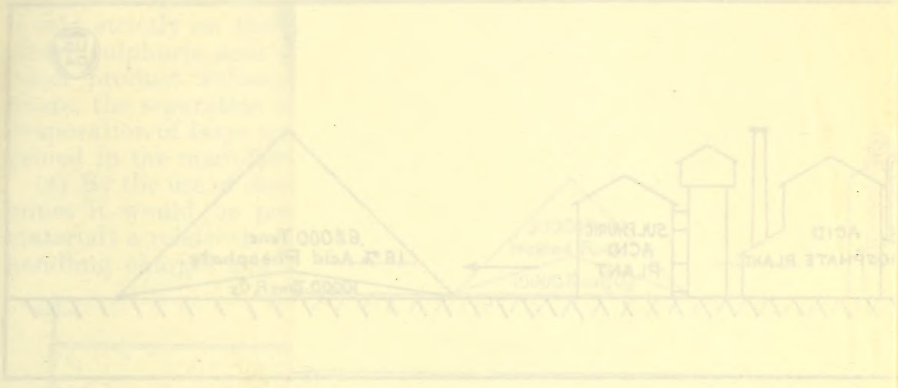
The pyrolytic process of producing phosphoric acid for fertilizer purposes appears to offer four distinct advantages over the sulphuric acid process even where the actual cost of the power or fuel required per unit of soluble P_2O_5 is somewhat greater than the cost of the sulphuric acid necessary to effect the same result.

(1) This process makes it possible to utilize low or medium grade phosphate deposits which are unfit for treatment with sulphuric acid, either because of their low content of P_2O_5 or their relatively high content of such impurities as oxides of iron and aluminum. Where the presence of 6 to 8 per cent of these impurities will cause a rock to be rejected as unsuitable for acid phosphate manufacture, this amount of alumina tends to aid rather than interfere with the reactions sought in the furnace process. Iron likewise, while very objectionable in the sulphuric acid process, causes no trouble in the furnace method other than its tendency to "fix" some of the phosphoric acid in the form of ferrophosphorus.[9] The formation of a certain amount of this compound, however, does not necessarily mean a loss, since it finds a ready market in the steel industry. The chief impurity in phosphate rock is usually silica, which is often present in such large amounts as seriously to dilute the acid phosphate made therefrom. Yet such phosphates may require further additions of sand in order to obtain the proper silica-lime ratio for successful treatment by the furnace process.

(2) The furnace method of treating phosphate rock makes it possible to dispense with the elaborate washing and screening processes now so extensively employed in Florida and Tennessee to separate the phosphate rock from the gangue or matrix in which it is embedded. As has been previously pointed out,[10] this mechanical separation involves the loss of a great deal of finely divided phosphate which would be practically all saved if the "run-of-mine" material were treated directly by the furnace scheme.

(3) The adoption of this method would largely eliminate the use of sulphuric acid which under present conditions is hauled to the fertilizer

[9] An alloy of iron and phosphorus containing as a rule from 10 to 20 per cent of the latter element.
[10] Phosphorus in Fertilizer, Yearbook, U. S. Department of Agr., 1920, p. 217.



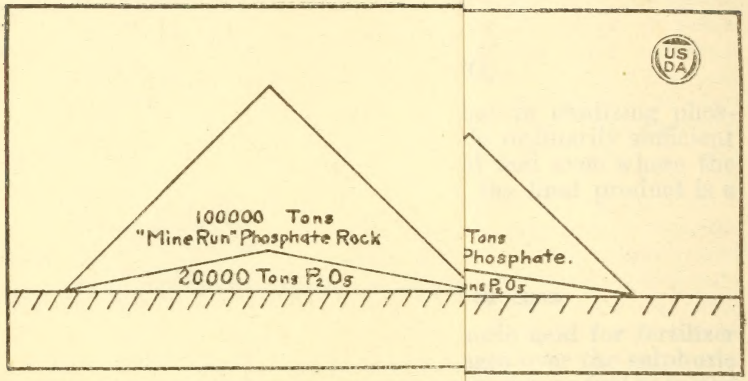


FIG. 1.—In the present method of preparing phosphati treated with an equal amount of sulphuri

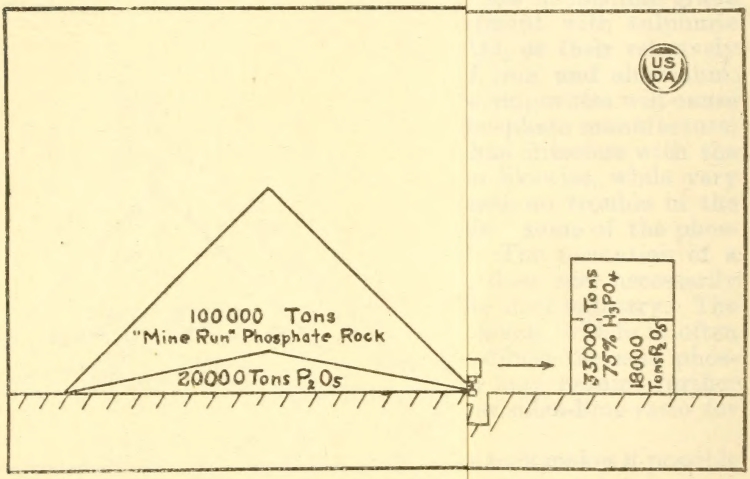


FIG. 2.—In the furnace method of preparing phosphoric a Assuming a 90 per cent efficiency in the furnace plant, the final product is a liquid conta number of concentrated products suitable for fertilizer use.

plants as acid and hauled away again as gypsum in acid phosphate. The chief function of this sulphuric acid is that of a reagent for converting the phosphate rock into a form which is quickly available to crops. In the manufacture of ordinary acid phosphate it dilutes by 50 per cent every ton of phosphate rock thus treated, forcing the ultimate comsumer to pay freight and handling charges on relatively valueless material. While it adds sulphur in the form of gypsum, which is recognized as a soil constituent essential for plant growth, it is sold strictly on the basis of its content of available P_2O_5. Even where sulphuric acid is used to produce phosphoric acid and this latter product subsequently employed to make double acid phosphate, the separation of the gypsum by filtration and the subsequent evaporation of large quantities of water tend to offset any advantage gained in the manufacture of a concentrated product.

(4) By the use of electric or fuel furnaces located near the phosphate mines it would be possible to produce (at the source of the raw material) a relatively concentrated product which would stand heavy handling charges and the cost of long freight hauls. This concen-

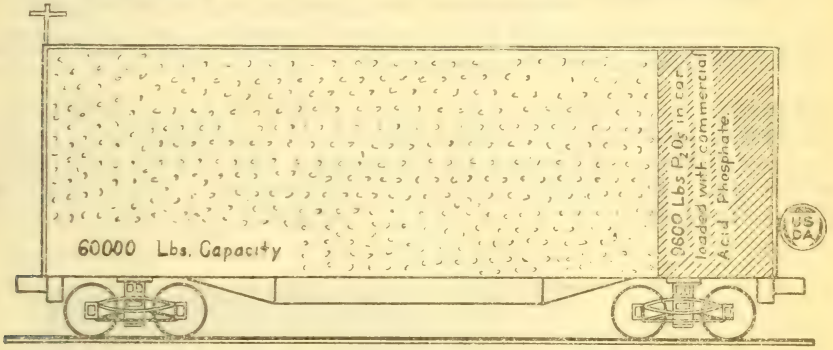


FIG. 3.—A car loaded to capacity (60,000 pounds) with 16 per cent acid phospate (the standard phosphate fertilizer of to-day) contains only 9,600 pounds of actual phosphoric acid (P_2O_5). Yet transportation and handling charges must also be paid on 84 per cent of gypsum and various impurities contained in this product. Our annual freight bill for transporting acid phosphate is fully $12,000,000.

trated product may be either strong phosphoric acid in liquid or crystallized form which can be shipped as such in lead-lined tank cars or wooden containers, double acid phosphate (containing from 40 to 50 per cent of soluble P_2O_5) made by treating phosphate rock with this strong phosphoric acid, ammonium phosphate which is produced by passing ammonia gas into phosphoric acid, or potassium phosphate which is formed by decomposing a potash salt such as muriate with phosphoric acid. In any event a product of the highest fertilizer value occupying but little storage or car space would be obtained which could be readily shipped and distributed at the least possible cost.

Figures 1 and 2 show graphically the saving in raw materials (and in the bulk of finished product) which may be effected by treating run-of-mine phosphate by the pyrolytic, or furnace, process instead of putting the material through a washing process and subsequently treating the washed rock with sulphuric acid. In Figures 3, 4, and 5 the economies which may be brought about by shipping these more concentrated products are illustrated.

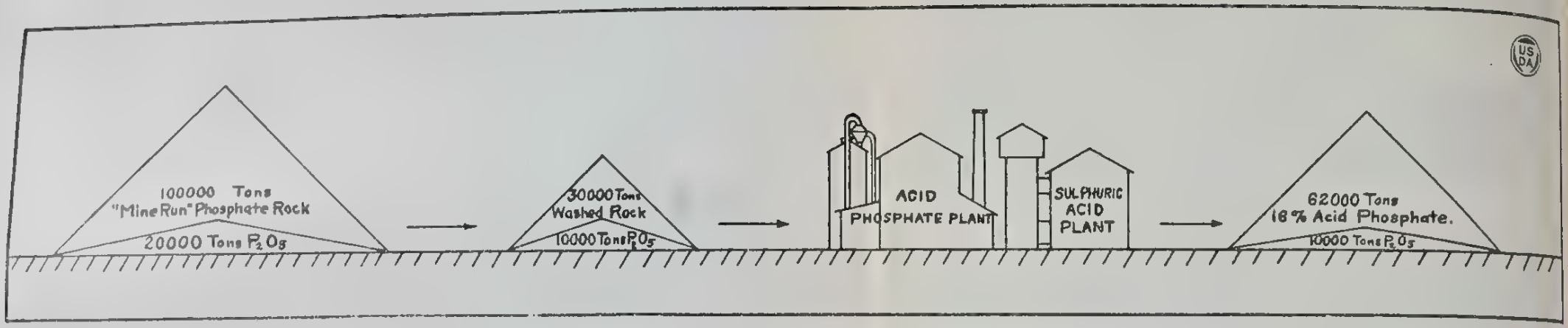


FIG 1.—In the present method of preparing phosphatic fertilizers only half of the phosphoric acid present in the deposit reaches the fertilizer factory in the form of washed rock. This rock is then treated with an equal amount of sulphuric acid and manufactured into acid phosphate—a product containing the same amount of phosphoric acid but in fully twice the bulk.

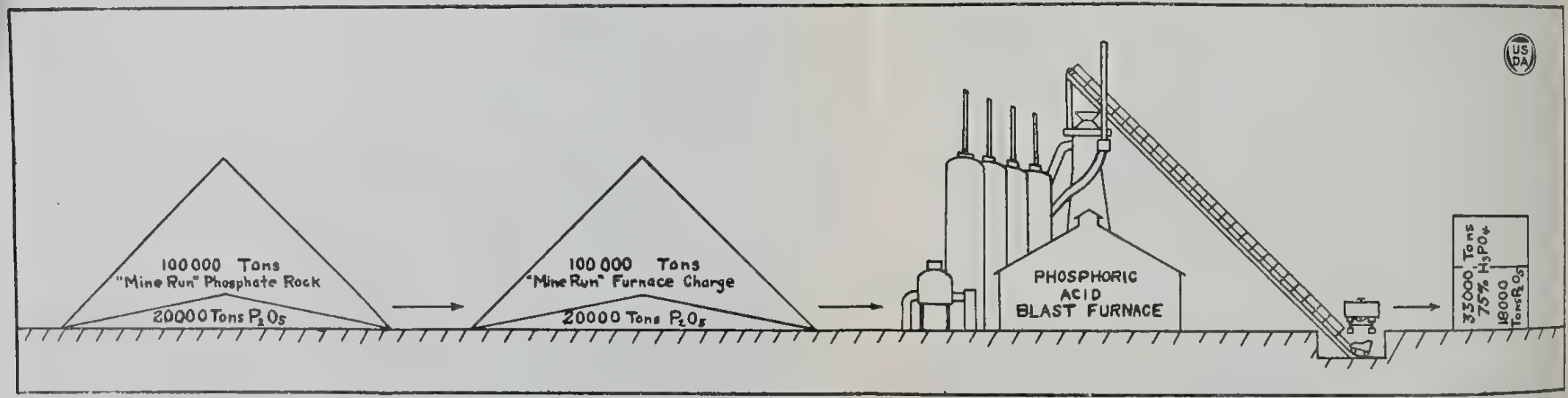


FIG. 2.—In the furnace method of preparing phosphoric acid the entire deposit of phosphate may often be utilized, and thus the losses of 50 per cent entailed in washing or purifying the rock eliminated. Assuming a 90 per cent efficiency in the furnace plant, the final product is a liquid containing nearly twice as much phosphoric acid (P_2O_5) as acid phosphate in a little more than half the weight. This acid may be manufactured into a number of concentrated products suitable for fertilizer use.

52670—23. (Face p. 5.)

A REVIEW OF METHODS FOR PRODUCING PHOSPHORUS AND PHOSPHORIC ACID BY VOLATILIZATION.

While the production of phosphorus has always depended on the volatilization of this element from its compounds under reducing conditions, in the early days of its manufacture the system employed was elaborate, cumbersome, and costly.[11] It involved, first, the

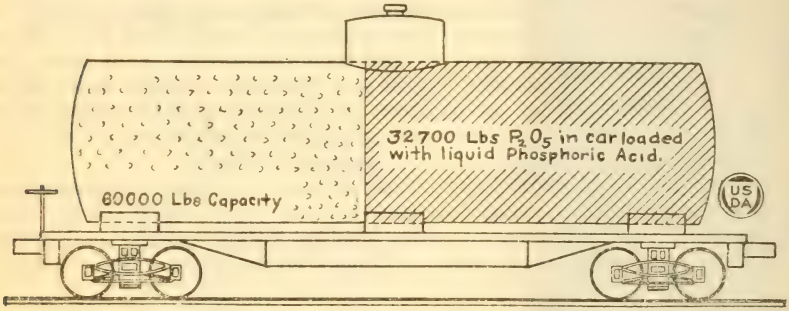


FIG. 4.—A car loaded to capacity (60,000 pounds) with liquid phosphoric acid (75% H_3PO_4) manufactured by the pyrolytic or furnace process contains 32,700 pounds of actual P_2O_5, or nearly three and one-half times as much as that in a car of acid phosphate.

treatment of phosphate of lime with sulphuric acid; second, the separation by filtration of the phosphoric acid thus obtained; third, the concentration of this acid by evaporation; and, fourth, the mixing of this acid with charcoal or coke and the heating of the mixture to high temperatures in clay retorts. Practically every step entailed

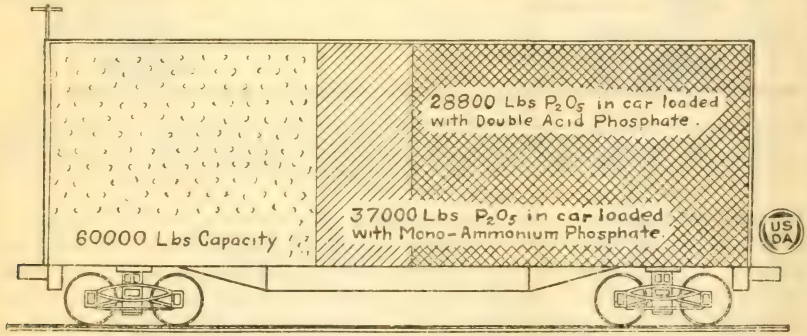

28800 Lbs P_2O_5 in car loaded with Double Acid Phosphate.
37000 Lbs P_2O_5 in car loaded with Mono-Ammonium Phosphate.
60000 Lbs Capacity
USDA

FIG. 5.—A car loaded to capacity (60,000 pounds) with either double acid phosphate or mono-ammonium phosphate contains from 28,800 to 37,000 pounds of actual P_2O_5, or from three to four times as much as that in a car of acid phosphate. By shipping our phosphoric acid (P_2O_5) in these concentrated forms an annual saving of from $8,000,000 to $9,000,000 in freight charges alone might be eventually effected on this fertilizer ingredient.

some loss of the material sought, so the recovery of the phosphorus was very incomplete.

Apparently the substitution of silica for sulphuric acid, so that phosphorus could be produced directly from phosphates of lime, was first proposed by Auberton and Boblique[12] in 1867, when these inventors took out a patent for volatilizing and collecting elementary

[11] Readman, J. B. An account of the Manufacture of Phosphorus. J. Soc. Chem. Ind. 9, p. 163 (1890).
[12] Readman, J. B. J. Soc. Chem. Ind. 9, p. 473 (1890).

phosphorus from pulverized mixtures of phosphate rock, sand, and coke heated to a high temperature in closed containers. Two years later (1870) Auberton[13] advocated the use of a blast furnace for fusing a mixture of phosphates, silica, and coke and driving off and collecting elemental phosphorus; and in 1879 Serve[14] took out a patent in which he proposes the use of blocks or bricks of an intimate mixture of phosphates and silica bound together by pitch, tar, or coal and smelted in a blast furnace.

The first process for volatilizing phosphoric acid recorded in this country is that of Giles and Shearer,[15] who took out a patent in 1888 for separating this acid from its impurities by passing a current of steam over the acid heated to redness. The distillate consisted of relatively pure phosphoric acid. In 1889 Readman[16] proposed to produce elementary phosphorus by heating in an electric furnace (from which air was excluded) a mixture of phosphorus-yielding material (in solution), sand, and coke. Two years later (1891) in an address before the Society of Chemical Industry[17] this inventor stated that he had found it was unnecessary to dissolve the phosphate mineral with sulphuric acid before furnacing, since a mixture of sand and coke decomposes it completely at the temperatures attained in the electric furnace. This general scheme is the one almost universally employed in the manufacture of phosphorus for matches and combustible products. In a general way the processes of Wing,[18] Duncan,[19] G. C. Landis,[20] and Haff[21] are similar to that proposed by Readman, since (with the exception of that of Wing[22]) they all deal with the production of phosphorus by smelting mixtures of phosphate rock, sand, and coke in an electric furnace. Wing and Landis, however, claim advantages for briquetted or molded charges on the basis that the temperature is more easily controlled, dust avoided, and a purer product recovered.

Ruymbeke[23] appears to have been the first in this country to patent a furnace process for the recovery of phosphoric acid rather than phosphorus. He advocates the use of a blast furnace for treating mixtures of phosphate rock, a reducing agent, and an acid flux, introducing into the upper part of the furnace sufficient air to oxidize any elemental phosphorus. In the processes of De Chalmot,[24] Maywald,[25] Levi,[26] Haff,[27] and Wilson and Haff[28] mixtures of phosphate rock and silica are heated in an electric furnace, but no reducing agent is added. The following reaction is assumed to take place:

$$Ca_3(PO_4)_2 + 3SiO_2 = P_2O_5 + 3CaSiO_3.$$

It is proposed to absorb the volatilized P_2O_5 in water to form H_3PO_4, and Levi[29] also suggests adding a salt of soda or potash to the residual slag in the furnace to make a soluble silicate.

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[13] Readman, J. B. J. Soc. Chem Ind. 9, p. 473 (1890).
[14] Idem.
[15] U. S. Patent No. 393428 (1888).
[16] U. S. Patent No. 417943 (1889).
[17] J. Soc. Chem. Ind. 10, p. 445 (1891).
[18] U. S. Patent No. 452821 (1891).
[19] U. S. Patent No. 733316 (1903).
[20] U. S. Patent No. 859086 (1907).
[21] U. S. Patent No. 1084856 (1914).
[22] This inventor proposes the use of a cupola furnace.
[23] U. S. Patent No. 540124 (1895).
[24] U. S. Patent No. 689286 (1901).
[25] U. S. Patent No. 902157 (1908).
[26] U. S. Patent No. 984769 (1911).
[27] U. S. Patent No. 1076497 (1913).
[28] U. S. Patent No. 1076499 (1913).
[29] Loc. Cit.

The experience of the writers, however, as well as that of a number of other investigators, has been that in the absence of a reducing agent very much higher temperatures must be employed to break the bond between the lime and phosphoric acid in the phosphate rock, and therefore it is poor economic practice to produce phosphoric acid without the addition of carbon or coke when such material can be obtained so cheaply.

Machalske [30] suggests that coke and an alkali metal chloride (sodium chloride) be mixed with the phosphate rock in the electric furnace, claiming that phosphorus chloride or hydrochloric and phosphoric acids are volatilized and sodium carbide is produced. He further claims that by introducing nitrogen sodium cyanide or cyanamid is obtained.

Haff [31] and Wilson and Haff [32] propose to heat feldspar and phosphate rock in an electric furnace to 2,000° C. without the addition of a reducing agent, claiming that phosphoric acid and potash are simultaneously evolved with the production of potassium phosphate according to the following equation:

$$3Al_2O_3.K_2O.SiO_2 + Ca_3(PO_4)_2 = 3Al_2O_3.CaO.SiO_2 + 2K_3PO_4.$$

These processes are open to the same objection as those of Maywald, Levi, and certain other processes proposed by Wilson and Haff in which no reducing agent is employed, and consequently very high temperatures are required.

Hechenbleikner [33] employs carbon or coke in addition to feldspar in smelting the phosphate charge, but it would seem to the writers that even under these conditions greater energy would be required to effect the chemical change indicated above, since potash is more readily volatilized from a basic and phosphoric acid from an acid slag. The economic possibility of employing silica in the form of greensand, potash shales, feldspar, or other potash-bearing silicates in the furnace process is very attractive, however, and this problem is now under investigation in this bureau.

With a view to producing compounds containing both phosphorus and nitrogen, Peacock [34] heats mixtures of phosphate rock and carbon in an atmosphere of nitrogen, claiming that phosphorus and carbonitrides are produced which can be converted into ammonia and ammonium phosphate by treatment with steam. No particular type of furnace is specified by this inventor. As far as known, however, there has been no commercial application of this process.

With a view to the simultaneous production of ferrophosphorus and phosphoric acid or other phosphorus compounds, J. J. Gray [35] proposes to smelt a mixture of phosphate rock, silica, coke, and iron ore in an ordinary blast furnace. The ingredients in the charge are so proportioned that while the maximum displacement of phosphorus from the phosphate rock is sought the amount of iron added in the form of ore is insufficient to take up all of the phosphorus thus evolved. Two blast furnaces for the production of ferrophosphorus are in operation in Tennessee, but in neither case is any elemental phosphorus or phosphoric acid recovered.

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[30] U. S. Patents Nos. 789438, 789439, 789440 (1905).
[31] U. S. Patent No. 1018186 (1912).
[32] U. S. Patent No. 1103910 (1914).
[33] U. S. Patent No. 1299337 (1919).
[34] U. S. Patents Nos. 1129514, 1129722 (1915).
[35] U. S. Patent No. 1168495 (1916).

Washburn[36] and Hechenbleikner[37] have each taken out a great number of patents dealing with processes for the volatilization of phosphoric acid and with types of furnaces in which the reactions may be brought about. Space forbids detailed discussions of all these methods and apparatus, but several which appear to have particularly interesting features are given below.

In Patent No. 1100639 (1914) Washburn proposes to charge a mixture of phosphate rock, silica, and carbonaceous material into the shaft of a blast furnace, where the combustion of the fuel is effected and the mass brought to a state of fusion. The molten material is then run into the crucible of an electric furnace, where the final smelting of the charge and complete volatilization of the phosphoric acid is accomplished. In Patent No. 1314229 (1919) he describes an apparatus in which are combined certain features of both the blast and electric furnace, and suggests a briquetted mixture of phosphate rock and silica in order to insure a free passage of the gaseous products through the charge in the shaft. Air is introduced into the shaft to burn the combustible gases and evolved phosphorus and thus preheat the green charge.

Both Hechenbleikner and Washburn describe furnaces[38] in which the charge is fed through a rotary kiln and the preheated or partially smelted mass then run into the crucible of an electric furnace, where coke or some other carbonaceous material is added and the remaining phosphoric acid is driven off. By leading the hot and burning gases through the kiln countercurrent to the phosphate charge, heat economies are effected which cut down the energy required in smelting the material in the electric furnace.

Other processes related to the volatilization of phosphorus and phosphoric acid are described in the public service patents taken out by Ross, Carothers, and Merz[39], Waggaman, and others[40].

THE USE OF THE ELECTRIC FURNACE IN THE VOLATILIZATION OF PHOSPHORIC ACID.

The first experimental work conducted in this bureau on the production of phosphoric acid by the volatilization process was carried on by Ross, Carothers, and Merz[41] in an electric furnace. A fair grade of sand and coke and a medium grade of Florida pebble phosphate were employed, these ingredients being mixed in such proportions as to react according to the first equation given on page 4 except that an excess of 20 per cent of both coke and sand were added over that theoretically required.

A furnace of very simple design was used in these early experiments. It consisted of an iron cylinder, 4 feet in diameter and 4½ feet high, lined with 9 inches of fire brick, and provided with a tap hole near the bottom for the removal of the slag. A three-phase alternating current was used, and this was stepped down from 220 volts by two single-phase 75 kilovolt ampere transformers. Each transformer was provided with a split primary, and by joining in different combinations in series and in parallel the coils in the secondary, volt-

[36] U. S. Patents Nos. 1000311 (1911); 1044957, 1047864 (1912); 1100639 (1914); 1149233 (1915); 1314229 (1919); 1359211 (1920); 1373471 (1921).
[37] U. S. Patents Nos. 1112211 (1914); 1167755, 1173960, 1202837 (1916), 1217306 (1917); 1299336, 1299337 (1919).
[38] U. S. Patents Nos. 1167755 (1916); 1299336, 1299337 (1919); 1359211 (1920).
[39] U. S. Patents Nos. 1283398 (1918); 1284200 (1918); 1329273 (1920).
[40] U. S. Patents Nos. 1241971 (1917); 1282994 (1918); 1334474 (1920); 1387817 (1921).
[41] Jour. of Ind. and Eng. Chem. 9, No. 1, p. 26 (1917).

ages varying from 40 to 100 in steps of 20 and also halves of these voltages were obtained. A view of this first furnace is shown in Plate I.

Practically complete volatilization of phosphoric acid from the mixtures given above was readily obtained, but during the preliminary stages of the work great difficulty was experienced in recovering the acid thus evolved, since its absorption in water can only be completely brought about by rather elaborate systems of sprays, baffles, or diving walls, and even then it is impractical to collect all of the P_2O_5 fumes in the form of strong phosphoric acid. These investigators, therefore, decided to try out the Cottrell method of electrical precipitation [42] for collecting the volatilized acid, and after a good deal of preliminary experimentation built a small plant which proved conclusively that this process could not only be successfully employed but possessed a number of advantages over the water-absorption system. This was the first time that the Cottrell precipitator was ever used for collecting a product purposely volatilized in order to apply this method of recovery.

Since this same precipitator was used in the early experiments conducted by the senior author of this bulletin, a quotation descriptive of the apparatus and its auxiliary equipment taken from the article of Ross, Carothers, and Merz [43] is given below.

COTTRELL ELECTRICAL PRECIPITATOR.

The power used in the precipitator was provided by a 110-volt, 60-cycle, alternating-current motor-generator set, and was stepped up by an 8 kilovolt ampere transformer capable of yielding voltages of 10,000, 20,000, and 40,000 volts. In these experiments the highest voltage only was used. From the transformer the current was changed to intermittent direct current by a small mechanical rectifier attached to the shaft of the generator and so adjusted as to operate in synchronism with it. The positive lead from the direct current side of the rectifier was earthed while the other terminal was connected to the wires suspended in multiple, one in each of the pipes used in the precipitator. Each pipe was then earthed.

In the preliminary experiments made with this precipitator, sheet-iron pipes were used, 6 inches in diameter and 10 feet high. The precipitated acid, however, had such a corrosive action on the pipes that they had to be abandoned. Pipes were then constructed from ordinary 6-inch glazed terra-cotta tile, five sections being taken for each pipe. The precipitated acid gave to the inside of the pipes an effective conductive surface and in grounding the pipes it was found sufficient simply to bring the ground wire to the inside surface of each pipe at one point. Arranged in this way the terra-cotta pipes could be used just as efficiently in the precipitation of the acid as metal pipes and they had the very important advantage of being unaffected by phosphoric acid. Wires of monel metal were found to be least acted upon when suspended in the pipes, but nichrome wire also served quite well. Weights were suspended at the ends of the wires and individual oscillations were prevented by a wire connecting all the weights. * * *

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[42] Lodge, Sir Oliver, The Electric Disposition of Dust, Smoke, etc., Jour. Soc. Chem. Ind. 5, p. 57 (1886); Cottrell, F. G., Electrical Precipitation of Suspended Particles, Jour. of Ind. and Eng. Chem. 3, p. 542 (1911); Strong, W. W., Electrical Precipitation of Suspended Matter in Gases, Jour. Franklin Institute 174, p. 239, Sept. 1912; Cottrell, F. G., Electrical Fume Precipitation, Trans. Amer. Inst. Min. Engrs. 43, p. 512 (1912); Cottrell, F. G. Problems in Smoke Fume and Dust Abatement, Smithsonian Institution, Report, 1913, p. 653, Publication No. 1307 (1914); Howard, W. H., Fume Precipitation at Garfield, Bul. Am. Inst. Min. Engrs. 49, p. 540 (1914); Nesbit, A. F., Theoretical and Experimental Considerations of Electrical Precipitation, Proc. Am. Inst. Elect. Engrs. 34, p. 507 (1915); Strong, W. W., Theory of Electrical Precipitation, Proc. Am. Inst. Elect. Engrs. 34, p. 220 (1915); Bradley, Linn, Practical Application of Electrical Precipitation, Proc. Am. Inst. Elect. Engrs. 34, p. 523 (1915); Shmidt, W. A., Cottrell Processes of Electrical Precipitation, Trans. Canadian Mining Inst., p. 110 (1915); Strong, W. W., Some Theoretical Aspects of Electrical Fume Precipitation, Trans. Am. Electro. Chem. Soc. 31, p. 415 (1917); Heimrod and Egbert, The Cottrell Processes in the Sulphuric Acid Industry, Chem Met. Eng. 19, p. 309 (1918); Gellert, N. H., Electrical Cleaning of Blast Furnace Gas, Blast Furnace and Steel Plant 7, p. 334 (1919); Landolt and Pier, Air Cleaning by the Cottrell Electrical Precipitation Processes, Bul. Am. Soc. of Heating and Ventil. Engrs., January (1920); Hesson, Landolt, and Heimrod, Recent Applications of the Cottrell Processes, Eng. and Min. Jour. 112, p. 446 (1921).

[43] Loc. cit.

The capacity of the fan used in drawing off the fumes from the furnace was 450 cubic feet per minute. As shown later, this flow of air was much in excess of that necessary to oxidize the phosphorus evolved from the furnace. Using a fan of this capacity it was found neccessary to use six pipes to bring about complete precipitation of the fumes. * * *

Since the phosphorus passes off from the furnace for the most part in the form of phosphorus pentoxide it might be expected at first thought that it would be collected as such in the precipitator. A simple calculation will show, however, that this is not practical, for there will always be enough moisture in the charge used and in the air required to oxidize the phosphorus evolved to convert the phosphorus pentoxide either in whole or in part into phosphoric acid. * * *

When the fumes were passed through the tower and precipitation thus made at a temperature but little above normal, the concentration of the acid first collected was in the neighborhood of 60 per cent phosphoric acid. * * * On cutting down the flow of air somewhat the concentration of the acid was increased to about 80 per cent, and it is quite evident that with the humidity of the air remaining the same a still more concentrated acid might be obtained by further limiting the flow of air through the furnace.

After the precipitator tower just described had been used intermittently for over two years it was found necessary to have one with a greater capacity, better suited to handle the gases (at a high velocity) evolved from a fuel-fired furnace. Accordingly the old treater of six (6-inch) terra-cotta pipes 14 feet long was torn down and a new one built containing nine pipes of the same dimensions; thus the capacity of the collector was increased approximately 50 per cent. In order to prevent the wires in the pipes from swinging in unison (a condition which at times caused considerable trouble in the old precipitator) the weights were not only fastened together with a grid but this grid was connected with a rigid horizontal bar (pipe) which passed through the center of a 6-inch terra-cotta pipe cemented into the side of the precipitator chamber. This bar in turn was anchored to an insulator outside of the tower. Such an arrangement did away with the frequent arcking encountered in the earlier experiments due to the swinging of the wires.

LARGER SCALE EXPERIMENTS.

The results obtained in the preliminary experiments with the electric furnace were so encouraging that it was deemed wise to continue the investigation on a larger scale in order to determine the commercial possibilities of the process. Accordingly a cooperative arrangement was entered into with several firms interested in this line of work and a plant of considerably larger capacity and much better suited for the purpose than that at Arlington Experimental Farm was erected at Hoboken, N. J. Protracted tests were made over a period of several days and weeks, and data obtained from which the cost of producing phosphoric acid by this method was estimated. This work was conducted under the direct supervision of J. N. Carothers, and a quotation from his article[44] describing the equipment is given below:

From the transformer ratings, the plant was a 200-kilowatt installation. The incoming power was quarter phase, 2,400 volts, which was transformed to 3 phase, 220 volts, by a bank of Scott connected tranformers. A second bank of transformers and a set of double-throw switches made it possible to have either 220 volts or 110 volts in the furnace. This arrangement was adopted so as to use the higher voltage for starting and the low voltage for operating. For the best operating conditions 110 volts were found satisfactory.

[44] Jour. Ind. and Eng. Chem. 10, No 1, p. 35 (1918).

The furnace consisted of a water-cooled crucible, with the cooled section extending no higher than the region of the molten slag. It was lined with fire-clay brick, but silica brick would prove more satisfactory. The portion not exposed to the action of slag was lined with a fire-clay brick. All gas mains and the cooling tower had a fire-clay brick lining. The heat from the gases served to harden the exposed surface and thus improve the service of the brick. The electrodes entered through the top of the furnace, but below a line where the charge entered. Care should be taken in the design of such furnaces that the angle of the electrodes conform with the angle of repose of the charge. Thus as the charge falls in a natural pile, the breakage of electrodes is eliminated. Electrodes may be conveniently controlled by hand, or mechanically. Hand control was used in this experiment, with the control so located that the switchboard and instruments could be observed. Six-inch and four-inch graphite electrodes were used. The life of a 4-inch electrode was about 7 days, while the 6-inch electrodes lasted on an average of 10 days under favorable conditions. Thus it may be seen that with such a low consumption electrodes may be operated by hand, since the chief movement of electrodes is when they are consumed. In this experiment the charge was fed by hand; however, this is obviously impractical in a large installation, where mechanical apparatus should be used. During regular operation about 2,000 pounds of rock were consumed per 12-hour period.

A slag pit filled with water was used to quench the molten slag as it flowed from the furnace. The slag thus chilled slid to one end and was removed mechanically. The P_2O_5 content of the slag was approximately 2 per cent, although it is possible to reduce it to 1.5 per cent or even 1 per cent for regular operation. The P_2O_5 content of the slag is largely a matter of the mixing of the charge and using the proper proportions of rock, sand, and coke.

The average production was 0.3 pound H_3PO_4 per kilowatt hour absorbed; however, there were periodic yields, during times of good operating conditons, in which 0.4 pound H_3PO_4 per kilowatt hour was produced. Judging from the average results of this experiment it seems reasonable to assume that a production of 0.6 pound H_3PO_4 per kilowatt hour is possible. Of course, the production is entirely dependent upon the efficiency of the furnace. In the case of this work no means were adopted to utilize the heat absorbed by the water surrounding the crucible or in the gases carried over from the charge. Also there were heat losses from the oxidation of phosphorus to phosphorus pentoxide (P_2O_5) and carbon monoxide (CO) to carbon dioxide (CO_2) which, if utilized, would materially have increased the efficiency of the process.

As the gases were removed from the furnace they passed through a cooling tower before entering the treater. This tower was installed to afford sufficient radiation, so that the gases entered the treater at 250° to 300° C. Above these temperatures in the treater electrical and mechanical difficulties arise which make higher temperatures undesirable.

The treater consisted of a header of common brick, with a reinforced concrete top to support the pipes, and 20 treater tubes of vitrified sewer pipes, 12 inches in diameter and 15 feet in length. All joints were packed loosely with silica to prevent air from entering at these points. The pipes were inclosed to prevent cracking, due to heat differences, and to maintain an even flow of gas.

All pipes at the top were inclosed in a common hood. Supports for the conductors rested on insulators within the treater hood. Complete clearance was given to 2,000 cubic feet of gas entering at 300° C., with a velocity of 3 linear feet per second. * * * Power was supplied the treater from a 150-volt motor-generator set, and transformed to higher voltages by a 7.5 kilovolt ampere transformer. A 5-point switch on the low-tension side of the transformer, connecting the various turns of coils, made a variation of voltages possible. It was found that 70 kilovolts was sufficient to give complete precipitation of the gases, at the above stated volumes and velocity.

As the acid fell from the pipes it was caught in a receiving basin of vitrified brick set in acid-proof cement. From this basin the acid flowed out and was disposed of by pumping to a receiving vat. The concentration of the acid collected was controlled by the temperature of the gas in the treater. At a temperature of less than 100° C. the concentration is not likely to exceed 50 per cent H_3PO_4, while a temperature of 250° to 300° C. will yield an acid of 85 to 93 per cent H_3PO_4. In one case an acid of 97 per cent was produced. An acid above 85 per cent H_3PO_4 will probably solidify when it reaches atmospheric temperatures, and therefore the pumping apparatus and pipe lines should be so constructed as to prevent clogging.

From the results obtained in this plant Carothers estimated the yield of phosphoric acid (P_2O_5) in a 3,000-kilowatt furnace operating

on a 24-hour basis 300 days of the year at 0.22 pound per kilowatt hour. Assuming that power was available at $25 per horsepower year he estimated the cost of production, exclusive of interest charges, maintenance, and depreciation, at 3.37 cents per pound of P_2O_5. While this cost compared rather favorably with that of the P_2O_5 in acid phosphate during the war, when the price of sulphuric acid was exceptionally high, the figures indicated that this process could hardly compete with the older method under normal conditions unless cheaper power or higher efficiency were obtained. But as Carothers has pointed out, there is little doubt that with a furnace of different design provided with means of recovering the heat in the effluent gases and utilizing the heat regenerated when the phosphorus is burned to P_2O_5 and the CO to CO_2, a considerably greater efficiency should be attained. Furthermore, the volatilized acid collected by the Cottrell precipitator can be used directly (without involving the expense of concentration) for treating high-grade phosphate rock in the production of double superphosphate, and thus the final cost of the unit of soluble P_2O_5 materially reduced.

Since these experiments were conducted, electric furnaces of commercial size for the simultaneous production of ferrophosphorus and phosphoric acid have been erected at Anniston, Ala., and are operating quite successfully. While most of the phosphoric acid produced at this plant is purified and sold for the purpose of manufacturing baking powder, and to the pure chemical trade, the president[45] of the company states that the experience gained during the last three years "clearly indicates that with cheap hydroelectric power and proper plant location phosphate rock can be smelted in the electric furnace for the production of fertilizer material at a cost comparing very favorably with the present method."

ELECTRIC SMELTING OF MINE-RUN PHOSPHATES.

But there is another factor equally if not more important than those just mentioned which has a direct bearing on the cost of the unit of P_2O_5 manufactured by the furnace process. This is the great saving which can be effected by employing low-grade and run-of-mine phosphates which are either unfit for treatment with sulphuric acid because of the inherent nature of the rock itself, or must be treated by some mechanical means to separate the phosphate from the impurities with which it is associated. With these facts in mind, the senior author undertook a number of experiments with the smaller electric furnace at Arlington Experimental Farm, Va., and while these tests were not conducted over any long period of time, they show that impure phosphates which can be readily and cheaply mined may be advantageously smelted in the electric furnace and the final product not only obtained more cheaply but a great conservation of our phosphate resources effected.

For this work samples of phosphate materials were obtained from each of the following three localities: (1) Mine-run phosphate from the hard-rock regions near Newberry, Fla.; (2) mine-run phosphate from the pebble fields near Fort Meade, Fla.; (3) Tennessee brown-rock phosphate from old dumps near Mount Pleasant, Tenn. The analyses of these samples of phosphatic material are given in Table 1.

[45] Jour. Ind. and Eng. Chem. 14, p. 630, (1922).

TABLE 1.—*Analyses of air-dried samples of mine-run and waste material from the Florida and Tennessee phosphate fields.*

Constituent.	Florida hard-rock and matrix.	Florida pebble phosphate and matrix.	Tennessee brown phosphate waste.
	Per cent.	*Per cent.*	*Per cent.*
CO_2	2.22	1.53	1.49
SiO_2	14.37	45.99	14.23
P_2O_5	30.69	15.38	29.85
$Al_2O_3+Fe_2O_3$	5.03	7.50	7.72
CaO	42.07	22.79	40.42
F	3.68	1.58	2.71
Total	98.06	94.77	96.42

Since the ratio of lime to silica used in the smelting experiments previously described was approximately 1 to 1.44, it will be seen from the analyses given in Table 1 that the samples of Florida hard-rock phosphate and matrix and Tennessee waste phosphates required further additions of sand, but that the mine-run Florida pebble had to be reinforced with higher grade phosphate rock in order to produce a charge suitable for furnace treatment. Further studies of the pebble phosphate deposits of Florida have shown, however, that the sample used in this case was probably exceptional, and that most of the run-of-mine material will require the addition of silica. In this particular instance, however, the mine-run pebble phosphate was reenforced with washed pebble rock containing 32 per cent of P_2O_5 and 7 per cent of SiO_2. The material from Florida hard-rock fields and that from the Tennessee dump heaps were mixed with high-grade white sand and sufficient coke was added in each instance to bring about the necessary reduction in the smelting operation. Approximately 500 pounds of each charge was made up and smelted in the electric furnace for three hours, the phosphoric acid volatilized being collected by means of the Cottrell precipitator employed by Ross, Carothers, and Merz. Since the charge used was relatively small and the duration of the tests comparatively short, no attempt was made to determine the quantity of P_2O_5 volatilized from the weight of acid collected by the precipitator, as there was of course a considerable loss in saturating the system. At the end of three hours, however, the furnace was tapped and the amount of phosphoric acid (P_2O_5) remaining in the slag was determined by analysis, that which was volatilized being figured by difference. The figures showing the efficiency of this furnace treatment as applied to mine-run rock are given in Table 2.

TABLE 2.—*Quantity of phosphoric acid (P_2O_5) volatilized from a charge made up of mine-run phosphates when smelted in the electric furnace for 3 hours.*

Phosphatic material used in charge.	P_2O_5 in charge exclusive of coke, CO_2, and F.	P_2O_5 in slag by analysis.	Proportion of total P_2O_5 remaining in slag after smelting.	Amount of P_2O_5 volatilized.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Hard-rock phosphate and matrix	22.0	0.50	1.8	98.2
Land-pebble phosphate and matrix	19.1	.66	3.0	97.0
Tennessee waste material	21.3	.67	2.7	97.3

The figures given in Table 2 show a volatilization fully as good as that obtained where high-grade phosphate rock was used, either at Hoboken, N. J., or in the preliminary experiments conducted in this same furnace. No data, however, were collected in this latter experiment that would admit of a comparison between the power consumed on the mine-run samples and that required for a charge made up of high-grade phosphate rock, sand, and coke, but it seems unlikely that there would be much difference in these figures since the extra power required to smelt the slight increase in the quantity of charge, due to the presence of iron and aluminum oxides and perhaps a little extra carbonate of lime, should be more than offset by the lowering of the melting point caused by the presence of these impurities. In the following tables are given the estimated costs of producing the unit of P_2O_5 by the two processes, namely, the sulphuric acid method and the furnace process, from various grades and types of phosphate rock in the form of phosphoric acid, acid phosphate, and double superphosphate.

TABLE 3.—*Estimated cost (at the mines) of producing 1 ton of available phosphoric acid (P_2O_5) by treating high-grade washed phosphate rock with sulphuric acid.*

Item.	Florida hard-rock phosphate.			Florida pebble phosphate.			Tennessee brown-rock phosphate.		
	Quantity.	Cost per ton.	Total cost.	Quantity.	Cost per ton.	Total cost.	Quantity.	Cost per ton.	Total cost
	Tons.			*Tons.*			*Tons.*		
Phosphate rock	3.18	$3.50	$11.13	3.18	$2.50	$7.95	3.18	$2.75	$8.75
Sulphuric acid (50° B.)	3.44	[1]8.00	27.52	3.44	[1]8.00	27.52	3.44	[1]8.00	27.52
Labor and repairs	.....	[2]1.30	8.61	.....	[2]1.30	8.61	.....	[2]1.30	8.61
Total cost per ton of P_2O_5	.....	.....	47.26	.....	.....	44.08	.....	.....	44.88
Total cost per unit of P_2O_5	.....	.....	.47	.....	.....	.44	.....	.....	.45

[1] Cost per ton, including interest, taxes, and insurance.
[2] Cost per ton of material handled.

TABLE 4.—*Estimated cost (at the mines) of producing 1 ton of phosphoric acid (P_2O_5) by the electric furnace method from high-grade washed phosphate rock.*

Item.	Florida hard-rock phosphate.			Florida pebble phosphate.			Tennessee brown-rock phosphate.		
	Quantity.	Cost per ton.	Total cost.	Quantity.	Cost per ton.	Total cost.	Quantity.	Cost per ton.	Total cost.
	Tons.			*Tons.*			*Tons.*		
Phosphate rock	3.32	$3.50	$11.62	3.32	$2.50	$8.30	3.32	$2.75	$9.13
Sand	1.50	.25	.37	1.50	.25	.37	1.50	.50	.75
Coke	.75	8.00	6.00	.75	8.00	6.00	.75	4.50	3.37
Operating expenses:									
Electrodes $2.13									
Labor 4.45	.....	.....	50.59	.....	.....	50.59	.....	.....	50.59
Power[1] 44.01									
Total cost per ton of P_2O_5	.....	.....	68.58	.....	.....	65.26	.....	.....	63.84
Total cost per unit of P_2O_5	.....	.....	.69	.....	.....	.65	.....	.....	.64

[1] Power at $25 per horsepower year.

TABLE 5.—*Estimated cost (at the mines) of producing 1 ton of available phosphoric acid (P_2O_5) in the form of double superphosphate by treating high-grade washed phosphate rock with phosphoric acid obtained by volatilization in the electric furnace.*

Item.	Florida hard-rock phosphate.			Florida pebble phosphate.			Tennessee brown-rock phosphate.		
	Quantity.	Cost per ton.	Total cost.	Quantity.	Cost per ton.	Total cost.	Quantity.	Cost per ton.	Total cost.
	Tons.			*Tons.*			*Tons.*		
Phosphate rock	0.98	$3.50	$3.43	0.98	$2.50	$2.45	0.98	$2.75	$2.69
P_2O_5 in form of 58° B. acid	[1].67	68.58	45.95	[1].67	65.26	43.72	[1].67	63.84	42.77
Labor and power	.....	[2]1.30	2.68	.....	[2]1.30	2.68	.....	[2]1.30	2.68
Drying	.....	[3].25	.52	.....	[3].25	.52	.....	[3].25	.52
Total cost per ton of P_2O_5	.....	.....	52.58	.....	.....	49.37	.....	.....	48.66
Total cost per unit of P_2O_5	.....	.....	.53	.....	.....	.49	.....	.....	.49

[1] Equivalent to 1.08 tons of H_3PO_4 (58° B.). [2] Cost per ton of material handled.

TABLE 6.—*Estimated cost (at the mines) of producing 1 ton of phosphoric acid (P_2O_5) by the electric furnace method from mine-run phosphates.*

Item.	Florida hard rock and matrix.			Florida pebble and matrix.			Tennessee brown phosphate waste.		
	Quantity.	Cost per ton.	Total cost.	Quantity.	Cost per ton.	Total cost.	Quantity.	Cost per ton.	Total cost.
	Tons.			*Tons.*			*Tons.*		
Phosphate and matrix	3.62	$0.50	$1.81	4.89	$0.50	$2.45	3.73	$0.75	$2.80
Washed pebble for reinforcing	.....	.....	.....	1.12	2.50	2.80	.....	.....	.....
Sand	1.64	.25	.41	.....	.....	.....	1.64	.50	.82
Coke	.75	8.00	6.00	.75	8.00	6.00	.75	4.50	3.37
Operating expenses (electrodes, labor, and power).	.....	.....	50.59	.....	.....	50.59	.....	.....	50.59
Total cost per ton of P_2O_5	.....	.....	58.81	.....	.....	61.84	.....	.....	57.58
Total cost per unit of P_2O_5	.....	.....	.59	.....	.....	.62	.....	.....	.58

TABLE 7.—*Estimated cost (at the mines) of producing 1 ton of available phosphoric acid (P_2O_5) in the form of double superphosphate by treating high-grade phosphate rock with phosphoric acid from mine-run material.*

Item.	Florida hard-rock phosphate.			Florida pebble phosphate.			Tennessee brown-rock phosphate.		
	Quantity.	Cost per ton.	Total cost.	Quantity.	Cost per ton.	Total cost.	Quantity.	Cost per ton.	Total cost.
	Tons.			*Tons.*			*Tons.*		
Phosphate rock	0.98	$3.50	$3.43	0.98	$2.50	$2.45	0.98	$2.75	$2.69
P_2O_5 in the form of 58° B. acid	[1].67	58.81	39.40	[1].67	61.84	41.43	[1].67	57.58	38.58
Labor and power	.....	[2]1.30	2.68	.....	[2]1.30	2.68	.....	[2]1.30	2.68
Drying	.....	[3].25	.52	.....	[3].25	.52	.....	[3].25	.52
Total cost per ton of P_2O_5	.....	.....	46.03	.....	.....	47.08	.....	.....	44.47
Total cost per unit of P_2O_5	.....	.....	.46	.....	.....	.47	.....	.....	.45

[1] Equivalent to 1.08 tons of H_3PO_4 (58° B.). [2] Cost per ton of material handled.

While the figures given in the foregoing tables are largely estimates, they are considered conservative and fair in so far as the costs of each process and type of material used compares with any other. Summing up the data given in these tables, we find that the cost of the unit of P_2O_5 obtained by the electric furnace process on the basis of Carothers's figures is considerably higher than the present cost of the phosphoric acid produced by the sulphuric acid method, but when the phosphoric acid obtained by the former method is used to manufacture double acid phosphate, the final cost of the unit of soluble P_2O_5 is brought down very materially.

When run-of-mine phosphate is treated in the electric furnace, however, the cost of the unit of P_2O_5 in the form of acid is far below that

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obtained by the same process using high-grade rock, and where the phosphoric acid obtained by smelting such low-grade materials is utilized in making double superphosphate, the final cost of the unit of P_2O_5 compares very favorably with that produced by the sulphuric acid method. At this point, however, the double superphosphate has a distinct advantage over the ordinary acid phosphate, in that it is so concentrated that it can be handled, shipped, and distributed at a minimum cost.

THEORETICAL HEAT BALANCES.

The data obtained in these experiments and given in Tables Nos. 3 to 7, inclusive, indicate that where phosphoric acid is produced in the electric furnace the main cost item is that of electric power. Where this electric energy is available at a price as low as $25 per horsepower year, the actual cost of power is over 70 per cent of the total charge against the ton of P_2O_5 in the form of H_3PO_4. With a properly designed furnace, however, and efficient auxiliary equipment for conserving the heat wasted in the ordinary crucible type of furnace, it should be possible to reduce the power cost per unit of phosphoric acid very materially. In Tables 8 and 9, modified from two prepared by George T. Southgate, formerly employed in this bureau, the heat balance of two electric furnaces for the production of phosphoric acid, one an open crucible and the other of the shaft type, are given. Certain assumptions were made in making up these tables, but the figures are considered conservative and comparable in so far as the relative heat economies are concerned. In both instances sufficient carbon is assumed to be present to reduce completely the phosphoric acid to elementary phosphorus and enough silica added to give a slag having the composition $CaSiO_3$.

TABLE 8.—*Theoretical heat balance of electric furnace of simple crucible type.*

[Capacity 10 tons P_2O_5 per day of 24 hours.]

Item No.	Actions affecting temperature.	Heat generated (plus).		Heat consumed (minus).	
		Thousands of kilogram-calories per ton[1] of P_2O_5.	Per cent of total.	Thousands of kilogram-calories per ton[1] of P_2O_5.	Per cent of total.
1	Absorbed by burden before fusion[2]				
2	Absorbed by burden in fusing[2]				
3	Absorbed by endothermic reactions in ore			4,100	36.1
4	Evolved by exothermic reactions in ore	420	3.7		
5	Evolved by oxidation of C to CO	1,140	10.0		
6	Evolved by oxidation of this CO to CO_2	2,660	23.4		
7	Evolved by oxidation of P to P_2O_5	2,850	25.0		
8	Removal of heat by cooling masonry			1,619	14.2
9	Removal of heat by slag[3]			1,707	15.0
10	Removal of heat by evolved gases (at 650°C)			2,350	20.6
11	Removal of heat by unburned CO[4]			1,600	14.1
12	Heat supplied by electric energy	[5]4,306	37.9		
	Total	11,376	100.0	11,376	100.0

Economy:[6]

In pounds P_2O_5 per kilowatt hour	0.44
In 2,000 pounds P_2O_5 per kilowatt year	1.30
In 2,000 pounds P_2O_5 per horsepower year	1.43
In over-all thermal efficiency, per cent	36.10

[1] Metric ton.
[2] Included in item 9.
[3] Including small amount removed by ferrophosphorus.
[4] Assuming one-third of CO unburned in furnace.
[5] 5,010 kilowatt hours.
[6] Production based on 90 per cent recovery of P_2O_5 in furnace charge.

TABLE 9.—*Theoretical heat balance of electric furnace, shaft type.*

[Capacity 10 tons P_2O_5 per day of 24 hours.]

Item No.	Actions affecting temperature.	Heat generated (plus).		Heat consumed (minus).	
		Thousands of kilogram-calories per ton[1] of P_2O_5.	Per cent of total.	Thousands of kilogram-calories per ton[1] of P_2O_5.	Per cent of total.
1	Absorbed by burden before fusion[2]				
2	Absorbed by burden in fusing[2]				
3	Absorbed by endothermic reactions in ore			4,100	44.1
4	Evolved by exothermic reactions in ore	420	4.5		
5	Evolved by oxidation of C to CO	1,140	12.3		
6	Evolved by oxidation of this CO to CO_2	2,660	28.6		
7	Evolved by oxidation of P_2 to P_2O_5	2,850	30.6		
8	Removal of heat by cooling masonry			2,369	25.5
9	Removal of heat by slag[3]			1,707	18.3
10	Removal of heat by evolved gases (at 315° C)			1,124	12.1
11	Removal of heat by unburned CO[4]				
12	Heat supplied by electric energy	[5]2,230	24.0		
	Total	9,300	100.0	9,300	100.0

Economy:[6]

In pounds of P_2O_5 per kilowatt hour	0.85
In 2,000 pounds P_2O_5 per kilowatt year	3.70
In 2,000 pounds P_2O_5 per horsepower year	2.77
In over-all thermal efficiency, per cent	44.10

[1] Metric ton.
[2] Included in item 9.
[3] Including small amount of ferrophosphorus.
[4] Assuming all CO burned in furnace crucible and shaft.
[5] 2,595 kilowatt hours.
[6] Production based on 90 per cent recovery of P_2O_5 in furnace charge.

It will be noted that under these conditions the over-all furnace reactions are exothermic. If, therefore, no heat were lost in the evolved gases, in unburned carbon monoxide, from radiation through the walls of the furnace, and in the slag which is tapped off, the reaction when started should go to an end without power consumption. Of course, some of these losses can not be avoided and others can only be partially eliminated, but as will be seen by comparing the figures for the two types of furnaces the efficiency of the shaft type, wherein much of the heat in the effluent gases is conserved and the phosphorus and CO are completely oxidized before leaving the furnace shaft, a great saving in power consumption may be effected.

With the development of certain power sites it is possible that electric energy may be obtained for purposes such as fertilizer production at a price much below $25 per horsepower year. This would make it feasible either to transport and use higher grade phosphate rock from the Florida fields or to transmit such power to the Tennessee phosphate fields and use run-of-mine phosphates, thus eliminating the costly washing process and conserving and utilizing deposits which are at present considered unfit for the production of phosphatic fertilizers. The map (fig. 6) graphically illustrates the distance between Muscle Shoals and the phosphate deposits of Tennessee.

THE USE OF THE FUEL FURNACE IN THE VOLATILIZATION OF PHOSPHORIC ACID.

At the present time, however, there is very little cheap electric power available in this country. Moreover, the history of our hydroelectric developments in the past has shown that the demand for

FIG. 6.

primary power for public utilities and for industries turning out relatively high-priced products has been so great that the manufacturer of lower-priced goods which depend upon smelting processes has had to look to fuel for his source of energy. Even should there be a great increase in our power developments, many believe that it

will still be economically unsound to dispose of this power for the manufacture of a material as cheap as phosphate fertilizer must always be.

COMPARATIVE COST OF THE THERMAL UNIT FURNISHED BY ELECTRIC POWER AND FUEL.

In the volatilization process of producing phosphoric acid, however, the chief function of the electric current is that of supplying the temperature necessary to effect the chemical reactions involved, and the electric furnace is merely a convenient type of apparatus to use in bringing about the decomposition of phosphate rock under reducing conditions. It logically follows, therefore, that if these same conditions can be fulfilled by employing fuel as a heating source in lieu of the electric arc, a great saving in the cost of the heat energy required should be effected. The following charts (figs. 7, 8, 9) and Table 10 give a fairly clear idea of how electric power and fuel compare in cost as sources of equivalent quantities of heat energy.

TABLE 10.—*Prices assumed for electric power and corresponding costs of standard fuels as sources of equivalent quantities of heat.*

Electric power[1] cost per kilowatt year.	Maximum prices at which standard fuels must be obtained to compete with electric power at rates given in column 1.			
	Coal[2] per long ton.	Fuel oil[3] per gallon.	Coke[4] per long ton.	Natural gas[5] per thousand cubic feet.
$5	$4.60	$0.022	$4.60	$0.18
10	9.20	.044	9.20	.36
15	13.80	.066	13.80	.54
20	18.40	.088	18.40	.72
25	23.00	.110	23.00	.90
30	27.60	.132	27.60	1.08
35	32.20	.154	32.20	1.26
40	36.80	.176	36.80	1.44

[1] 3,415 B. t. u. per kilowatt hour.
[2] 14,000 B. t. u. per pound.
[3] 19,000 B. t. u. per pound.
[4] 14,000 B. t. u. per pound.
[5] 1,200 B. t. u. per cubic foot.

In the curves given in Figure 7 the cost of a million British thermal units produced by certain standard fuels at various prices is compared with the cost of the heat equivalent produced by electric power at various rates per kilowatt hour.

In Figure 8 curves are given for converting the cost of the thermal unit from mills per kilowatt hour into the terms of dollars per kilowatt year or dollars per horsepower year, either of which is a more conventional method of expressing the cost of power which is consumed in large blocks.

In Table 10 certain points along the curves given in Figure 7 are taken in order to show typical examples of the prices at which electric power must be obtained to compete with fuel furnishing the same number of thermal units.

In Figure 9 a comparison is made of the yield of product obtained by burning 1 pound of various fuels with that obtained by a power

consumption of 1 kilowatt hour. This last chart is drawn up on the assumption that the same efficiency in utilization of thermal

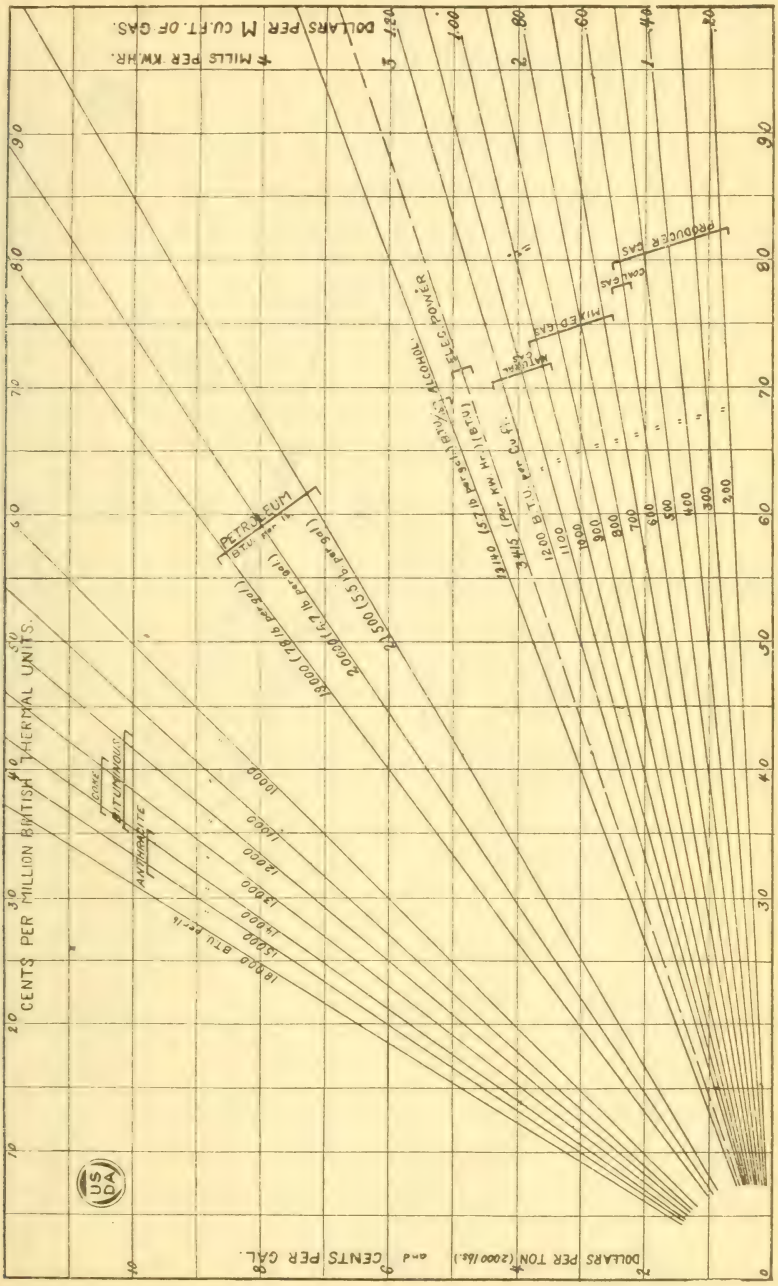


FIG. 7.—Comparative costs of 1,000,000 British thermal units furnished by electric power and certain standard fuels.

units is attained from both sources of heat energy which (as pointed out below) is not strictly true.

It is evident that under present conditions the cost of the heat unit produced by the hydroelectric developments in this country can

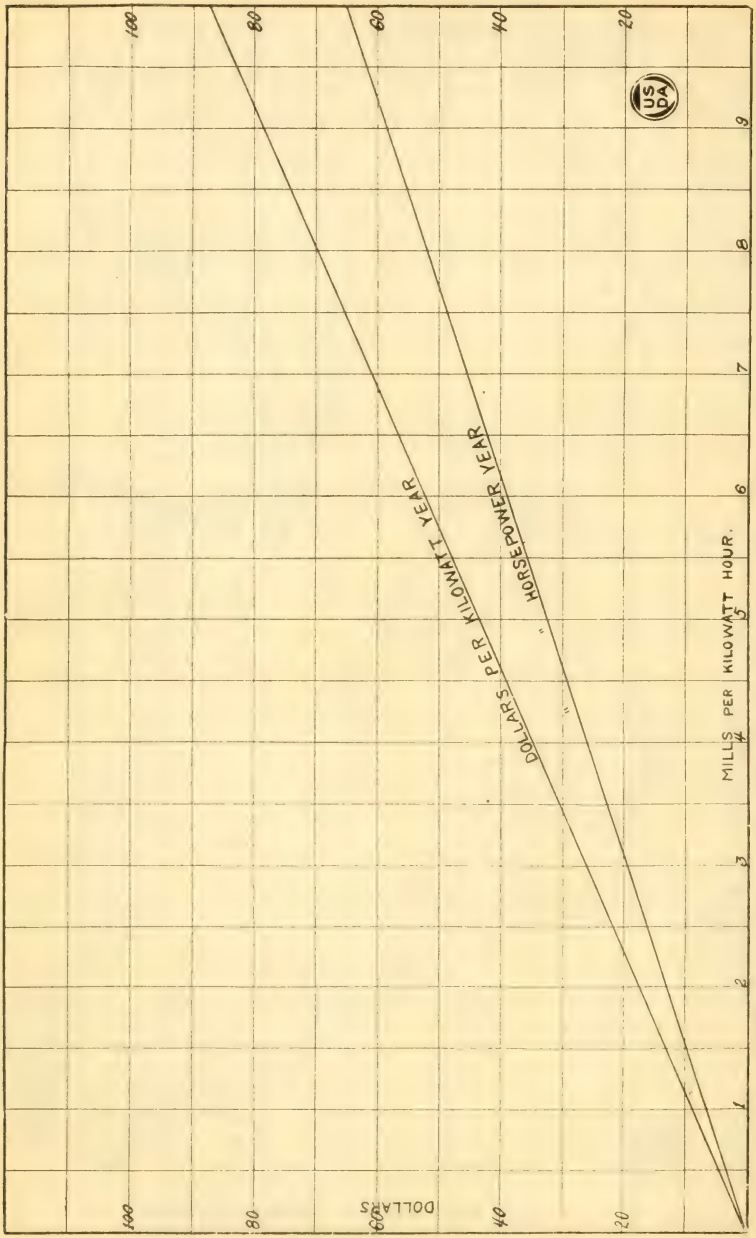


FIG. 8.—Chart for converting power costs from mills per kilowatt hour into dollars per kilowatt year and horsepower year.

not compare in cheapness with that obtained by the use of either fuel oil, coal, or coke. It is not altogether fair, however, to compare the

efficiency of electric power with that of fuel as a heating source on the basis of the actual cost of the thermal unit developed by each. In

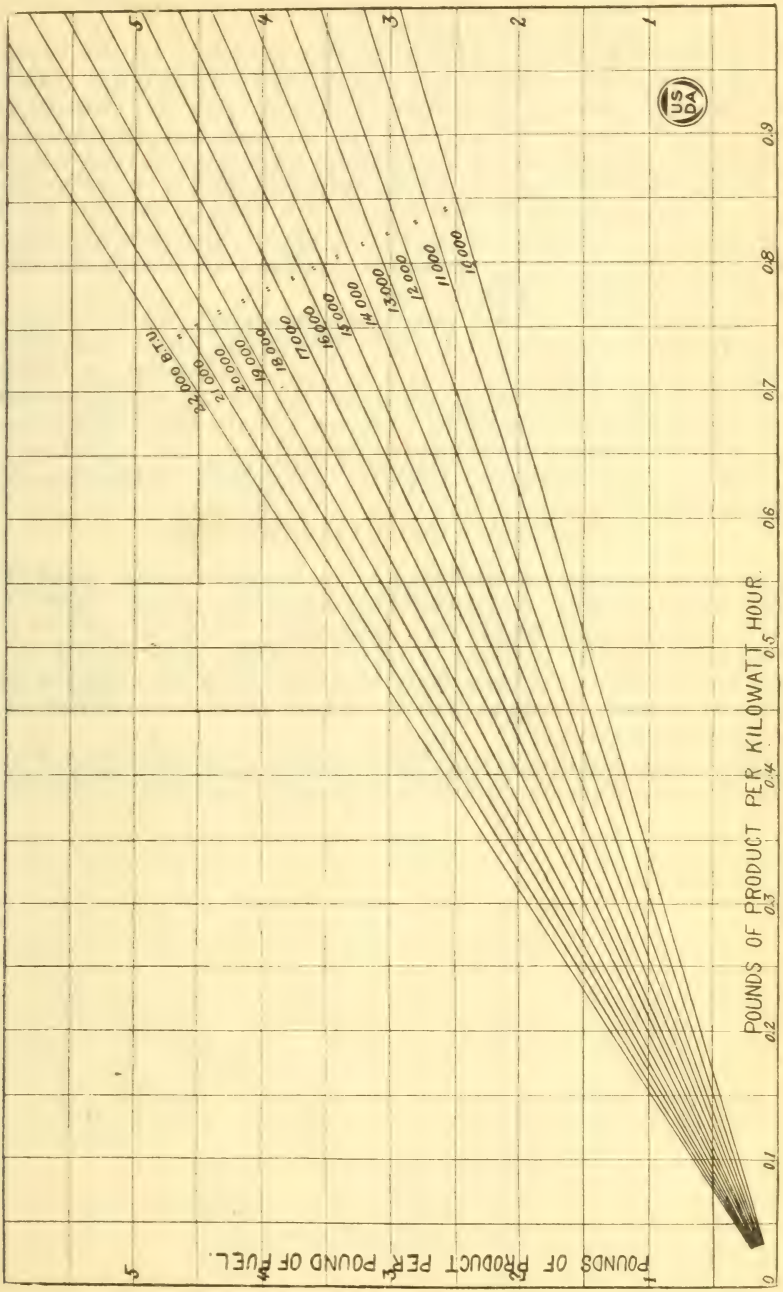


FIG. 9.—Comparison of yield per kilowatt hour with yield per pound of fuel of various thermal values.

the electric furnace the heat is very much more localized, and there is less loss through radiation, and in the evolved gases, than in a

furnace heated by fuel, where excess air must be introduced for combustion. By proper regenerative apparatus and means of utilizing the sensible heat in the effluent gases, however, this latter loss of valuable heat may be materially reduced.

To further offset the probable greater efficiency of the thermal unit developed by electric energy it must be borne in mind that the utilization of mine-run phosphates depends upon the location of a furnace plant close to the source of the raw material (the phosphate mines), and while certain of the phosphate deposits of Tennessee are sufficiently close to admit of the transmission of power to the mines from a development at Muscle Shoals, the Florida deposits are far removed from any possible source of cheap hydroelectric power. Low-priced fuel, however, is readily available in practically all of the phosphate fields of this country.

With these facts in mind the writers undertook an investigation to determine if complete elimination of phosphoric acid from proper mixtures of phosphate rock, sand, and coke could not be brought about at the temperatures attained and under the conditions existing in various types of fuel-fired furnaces, and the results have shown that this can be done by properly proportioning the ingredients in the charge and maintaining reducing conditions within the phosphate mass.

PRELIMINARY LABORATORY EXPERIMENTS.

The work was first undertaken on a laboratory scale using relatively pure samples of tricalcium phosphate, quartz flour, and carbon. These ingredients were thoroughly mixed in several proportions, placed in graphite or clay crucibles, and heated in an injection furnace for various periods of time with the crucibles both open and closed. City gas and a cold-air blast were employed in heating these mixtures.

Table 11 shows in part, the results obtained by heating such mixtures with and without the addition of small amounts of aluminum oxide.

TABLE 11.—*Volatilization of phosphoric acid from mixtures of tricalcium phosphate, silica, coke, and alumina, by smelting in open and closed crucibles in a dental furnace using illuminating gas and an air blast.*

Sample.	Crucible.	Proportions of materials used in charge.				Percentage composition.					Temperature attained.	Length of time heated.	P_2O_5 in slag.	Proportion of P_2O_5 volatilized.	Character of slag.
		$Ca_3(PO_4)_2$.	SiO_2.	Al_2O_3.	Coke.	SiO_2.	CaO.	Al_2O_3.	P_2O_5.	C.					
		Grams.	*Grams.*	*Grams.*	*Grams.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*°C.*	*Hours.*	*P. ct.*	*P. ct.*	
12 A	Closed (clay)	20.0	16.6	.....	5.2	40.7	25.9	0.7	21.9	10.8	[1] 1,400	0.75	3.24	89.8	Fluid, grayish black.
12 G	Open (clay)	20.0	16.6	.....	5.2	40.7	25.9	.7	21.9	10.8	[1] 1,400	1	7.20	76.2	Viscous gray, white bloom on surface.[2]
12 N (1)	Open (graphite)	20.0	16.6	6.6	5.2	35.1	22.4	14.3	18.9	9.3	1,200	1	4.92	80.4	Viscous black.
12 N (2)	do	20.0	16.6	6.6	5.2	35.1	22.4	14.3	18.9	9.3	[1] 1,400	2	None.	100.0	Fluid, black.
12 O	Open (clay)	20.0	16.6	.....	4.8	41.1	26.2	.7	22.1	9.9	[1] 1,100	1	3.36	89.3	Fluid, light gray.
12 P	do	20.0	16.6	6.6	5.0	40.9	26.1	.7	22.0	10.3	[1] 1,400	1	2.22	93.0	Fluid, light gray, bloom on surface.[2]
12 Q	do	20.0	16.6	6.6	5.4	40.7	25.8	.7	21.8	11.0	[1] 1,400	.75	4.65	84.9	Do.[2]
12 R	do	20.0	16.6	6.6	5.6	40.5	25.7	.7	21.7	11.4	[1] 1,400	.75	2.45	92.2	Do.[2]
12 (1)	do	20.0	16.6	6.6	5.2	40.7	25.9	.7	21.9	10.4	1,300	1	Trace.	100.0	Fluid, light gray, large bloom.[2]
12 (2)	Closed (clay)	20.0	16.6	6.6	5.2	40.7	25.9	.7	21.9	10.4	1,300	1	Trace.	100.0	Fluid, all slag.
12 (11)	Open (clay)	20.0	16.6	2.0	5.6	38.7	24.5	5.2	20.7	10.9	1,300	1	5.28	81.3	Viscous light gray; bloom on surface.[2]
12 (12)	Closed (clay)	20.0	16.6	2.0	5.6	38.7	24.5	5.2	20.7	10.9	1,300	1	1.91	93.6	Viscous dark; no bloom.
12 (15)	Open (clay)	20.0	20.0	2.0	4.8	43.6	23.2	4.9	19.6	8.7	1,300	1	4.26	83.7	Viscous gray; large bloom.[2]
12 (16)	Closed (clay)	20.0	20.0	2.0	4.8	43.6	23.2	4.9	19.6	8.7	1,300	1	3.52	86.6	Viscous gray; no bloom.
12 (17)	Open (clay)	20.0	22.0	2.0	4.8	45.9	22.2	4.7	18.8	8.4	1,300	1	3.90	84.3	Viscous gray; large bloom.[2]
12 (18)	Closed (clay)	20.0	22.0	2.0	4.8	45.9	22.2	4.7	18.8	8.4	1,300	1	3.75	84.8	Viscous gray; no bloom.

[1] Above.

[2] An analysis of the bloom or white crust on the surface of slag obtained in open crucibles shows a considerably higher percentage of phosphoric acid than in the original mixture. The proportion of lime to phosphoric acid coincided very closely with that in calcium pyrophosphate ($Ca_2P_2O_7$).

An inspection of Table 11 shows that as a rule considerably better results were obtained where the crucibles were kept covered so that the oxidizing gases were not allowed to come in contact with the charge. In most instances where a molten slag was obtained and the heating continued sufficiently long, a very high percentage of the phosphoric acid contained in the charge was volatilized. When the crucibles were left open, however, it was noticed that a thick white crust or "bloom" usually formed over this slag and unless the temperature was raised to the point where the fire-clay crucible itself fused, this crust gave no sign of melting into the slag beneath. The amount of this crust in a number of instances was fully as great as that of the underlying slag and showed upon chemical examination a higher percentage of phosphoric acid than that present in the original mixture. The ratio of lime to phosphoric acid in this unfused material conformed closely to the ratio of these ingredients in calcium pyrophosphate. Apparently under the oxidizing conditions existing at the surface of the mass the phosphoric acid distilling from the interior of the charge was fixed at the surface, producing calcium pyrophosphate according to the following equation:

$$2Ca_3(PO_4)_2 + P_2O_5 = 3Ca_2P_2O_7.$$

It was found, however, that when the crucibles were kept covered until the fusion was well under way and the carbon or coke thus protected in the molten slag the covers of the crucibles could be removed without the formation of this crust, and the reaction continued to an end in spite of the oxidizing conditions at the surface of the slag. The addition of small quantities of alumina to the charge contributed somewhat to the fluidity of the slag, it being a well-known fact that the presence of this substance in small amounts lowers the melting point of both acid and basic slags.

In these preliminary experiments the ratio of silica to lime was approximately 61 to 39, which is very close to the proportions of these ingredients in calcium trisilicate ($Ca_2Si_3O_8$). Charges having this silica-lime ratio gave slags from which a quicker and more complete evolution of P_2O_5 was obtained than from those of a less acid nature. Such slags, however, congeal so readily that the tapping of the furnace is rendered somewhat difficult. Subsequent experiments indicate that the more nearly neutral slags are more readily fused and probably better adapted for actual furnace operation.

These laboratory experiments pointed conclusively to the importance of maintaining reducing conditions in the phosphate charge until fusion has taken place, and it appeared at first that the most feasible method of doing so in a mass containing much finely divided material, such as the pebble phosphates of Florida or the run-of-mine phosphates from Tennessee, was by the indirect heating of the charge so that the oxidizing gases from the burning fuel would not come in contact with the reacting mass until the latter was brought to a molten condition. Accordingly, a fire-brick furnace of semicommercial size, of the type shown in Figure 10 and described by the senior author and others in United States Patents Nos. 1241971 and 1282994, was constructed at Arlington Experimental Farm, Va. This furnace comprised a central or inner chamber (holding about 150 pounds of charge) open both at the top and the bottom but constricted somewhat at the lower end to prevent the charge from working through

too rapidly. This chamber was supported by arches of carborundum brick above a hollow hearth intended to receive the molten silicate. The whole was surrounded by an outer chamber into the opposite walls of which were first set water-cooled tuyeres to deliver preheated air for the combustion of the coke as the charge descended upon the hollow hearth. These tuyeres, however, were later replaced by two oil burners so arranged that their flames played upon and around the lower part of the inner chamber, heating the charge by radiation through the 4½-inch walls. Any fumes which were evolved from the fusing mass were to be drawn down through the charge chamber into the outer chamber and passed, together with the gases of combustion, into the Cottrell precipitator previously described.

This indirect method of heating the charge, however, was so inefficient that after several trials, lasting from 18 to 24 hours each, it was abandoned as impractical. Little or no slag was obtained and only a relatively small quantity of phosphoric acid was driven off from the sintered product.

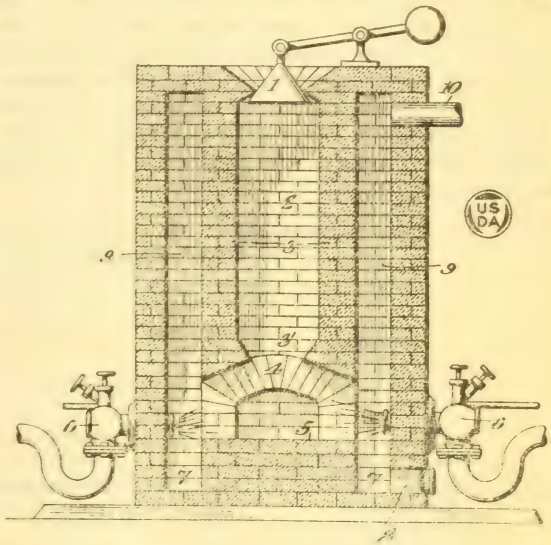


FIG. 10.—Vertical section of oil-burning furnace in which the first large scale experiments on the volatilization of phosphoric acid were conducted.

These experiments showed clearly that in order to make the process economically practical the calorific power of the fuel must be more completely utilized, which could only be done by the direct heating of the mass. This conclusion, however, complicated the problem of how to maintain the reducing conditions necessary for the volatilization of the phosphoric acid when the maximum efficiency of the crude-oil flame or that of any other fuel can only be attained under oxidizing conditions. The most promising type of furnace for this purpose seemed to be a modification of the blast furnace, wherein sufficient coke is used to maintain a reducing atmosphere both in the crucible and in the shaft. The run-of-mine phosphates with which the experiments were being conducted, however, are of such a character that it is impossible to handle them in a plant of the blast-furnace type, because of the large percentage of finely divided material present in the mass, through which it is impossible to force a draft.

THE BRIQUETTING OF MINERAL PHOSPHATES.

Accordingly experiments were undertaken with a view to briquetting the mixtures of finely ground pebble phosphate, sand, and coke, using various binders, such as magnesium chloride, calcium chloride, sodium fluoride, sodium silicate, phosphoric acid, acid sludge from

the refining of petroleum, and small percentages of starch. Briquets of several sizes were produced under pressures varying from one-half to 1 ton per square inch, but none of these binders proved very satisfactory, either because of the difficulty in removing the briquet intact from the machine, or because of the readiness with which the briquet shattered. Sulphite pitch, however, which is a by-product of the paper industry, proved to be a good binder when added to the finely ground mixtures in amounts above 5 per cent, though this material adds quite appreciably to the cost of the briquets.

In both Florida and Tennessee, however, many phosphate deposits in their natural state contain much soft phosphate and claylike material of considerable plasticity, and it was thought that the binding qualities of this run-of-mine phosphate might prove sufficiently effective to produce satisfactory briquets without the addition of an artificial binder. Since the binding capacity of this run-of-mine material depends largely on the amount of finely divided material or clay contained therein, the samples obtained from the various phosphate deposits in these two States were ground to 15 mesh in a small gristmill and then submitted to the mechanical analysis ordinarily employed in the classification of soils. In Table 12 are given the results of these analyses along with the analysis of very finely ground washed pebble phosphate of the grade used in the production of an average acid phosphate.

TABLE 12.—*Location, description, and mechanical analyses*[1] *of phosphates used in briquetting experiments.*

Sample No.	Location.	Thickness of stratum.	Description.	Sand, 1.0–0.05 millimeter.	Silt, 0.05–0.005 millimeter.	Clay, 0.005–0.0000 millimeter.
				Per ct.	*Per ct.*	*Per ct.*
1	Charleston, S. C., Mining & Manufacturing Co., Fort Meade, Fla.	15 feet+	Washed pebble phosphate.	45.2	36.0	18.8
2	Cummer Lumber Co., Newberry, Fla.	do	Mine-run phosphate	45.0	21.0	34.0
1-F	Downing Phosphate Co., Bartow, Fla.		do	56.2	7.6	36.2
1-F (2)	Downing Phosphate Co., near Mulberry, Fla.	20 feet+	Mine-run pebble phosphate.	84.3	5.8	9.9
4-F	do	do	do	78.5	7.2	14.3
1-T	Consolidated Phosphate Co., Hickman County, Tenn.	6 feet	Brown phosphate containing lump rock.	73.3	14.6	12.1
3-T	Deposit near Gallatin, Tenn.	4 feet	Brown disintegrated phosphate.	54.1	18.3	27.6
4-T	do	do	Similar to No. 3-T	55.4	17.6	27.0
6-T	Ruhm Phosphate Co., Mount Pleasant, Tenn.	5 feet	Brown phosphate containing lump rock.	66.2	16.1	17.7
7-T	do	7 feet	do	59.0	16.8	24.2
8-T	do	14 feet	Sample from upper end of waste pond.	42.5	39.0	18.5
9-T	do	15 feet	Sample taken 63 feet from 8-T.	24.2	50.2	25.6
10-T	do	10 feet 3 inches	Sample taken 63 feet from 9-T.	30.4	45.8	23.8
11-T	do	5 feet 11 inches	Sample taken 63 feet from 10-T.	11.6	56.7	31.7
12-T	do	5 feet	Sample taken 63 feet from 11-T.	22.5	41.1	34.4
13-T	do	4 feet 6 inches	Sample taken 63 feet from 12-T.	7.2	44.0	48.8
14-T	Charleston (S. C.) Mining Co., Wales, Tenn.	10 to 20 feet	Brown disintegrated phosphate.	50.4	20.4	29.2

[1] Mechanical analyses made according to the method employed in this bureau for the classification of soils.

TABLE 12.—*Location, description, and mechanical analyses of phosphates used in briquetting experiments*—Continued.

Sample No.	Location.	Thickness of stratum.	Description.	Sand, 1.0–0.05 millimeter.	Silt, 0.05–0.005 millimeter.	Clay, 0.005–0.0000 millimeter.
				Per ct.	*Per ct.*	*Per ct.*
15–T	International Agricultural Corporation, Wales, Tenn.	10 to 20 feet	High-grade disintegrated phosphate.	51.6	18.4	30.0
16–T	do	do	Low-grade disintegrated phosphate.	53.7	13.8	32.5
18–T	Federal Chemical Co., Ridley, Tenn.	6 to 10 feet	Mine-run brown phosphate.	46.5	19.7	33.8
19–T	do	do	do	62.4	16.6	21.0
20–T	do	do	do	52.6	22.4	25.0

It will be noticed that with few exceptions all of the samples of run-of-mine phosphates contained in their natural state much higher percentages of very finely divided material or clay than the high-grade washed pebble phosphate (Sample No. 1) even though the latter was ground in a ball mill for a considerable length of time. While most of these samples would yield excellent briquets when 7 to 10 per cent of water was added and the material submitted to a pressure of from one-half to 1 ton per square inch, the ultimate mechanical composition of a charge suitable for furnace treatment depends upon the amount of sand or higher grade phosphate which must be added to give the proper silica-lime ratio for the evolution of phosphoric acid at high temperatures. In Table 13 are given the chemical analyses of these samples and the quantities of sand or high-grade rock which must be added to give a silica-lime ratio of 59 to 41, which was the proportion used in the earlier work conducted on a semicommercial scale.

TABLE 13.—*Partial chemical analysis and silica-lime relations of natural phosphates.*

Sample No.	Chemical analysis.						Ratio, SiO_2 : CaO.	Quantity of sand or high grade rock to be added to 100 parts of material to give ratio SiO_2:CaO = 59.0 : 41.0 = 1.439.	
	SiO_2.	CaO.	P_2O_5.	Fe_2O_3.	Al_2O_3.	Total.		Sand.	Rock.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*		*Parts.*	*Parts.*
1[1]	6.85	44.78	31.09	1.48	2.13	86.33	0.153	57.36	.....
2	32.79	26.47	21.43	.....	[2]11.78	92.47	1.239	5.00	.....
1–F	26.96	29.05	23.61	2.09	8.40	90.11	.928	14.85	.....
1–F (2)	37.57	29.70	21.52	.....	[2]3.92	92.71	1.265	5.20	.....
4–F	45.20	24.29	18.36	.....	[2]4.91	92.76	1.861	.....	17.70
1–T	10.00	42.66	31.86	3.26	3.90	91.68	.232	51.35	.....
3–T	30.23	28.17	22.03	4.06	6.94	91.43	1.073	10.27	.....
4–T	38.74	23.00	17.88	4.45	5.00	89.07	1.686	.....	8.20
6–T	15.53	38.32	27.68	3.56	4.33	89.42	.405	39.65	.....
7–T	18.69	33.09	25.20	4.84	5.54	87.36	.565	28.91	.....
8–T	49.60	18.24	14.21	3.76	4.73	90.54	2.717	.....	33.9
9–T	58.94	12.20	10.23	4.30	5.06	90.73	4.830	.....	60.1
10–T	56.32	15.16	12.05	3.98	4.41	91.92	3.716	.....	50.0
11–T	66.81	8.05	6.92	4.46	6.82	93.06	8.300	.....	80.0
12–T	55.68	12.58	10.51	4.78	7.85	91.40	4.430	.....	54.5
13–T	61.18	6.60	6.32	5.68	9.57	89.34	9.275	.....	74.8
14–T	23.42	30.78	22.70	5.22	7.40	[2]89.52	.762	20.85	.....
15–T	22.26	31.41	23.85	4.78	7.79	90.09	.708	22.94	.....
16–T	57.34	12.00	11.23	4.90	7.23	92.70	4.775	.....	58.0
18–T	23.86	30.26	22.76	4.55	8.40	89.83	.788	19.64	.....
19–T	16.50	37.41	25.84	3.02	5.50	88.27	.441	37.33	.....
20–T	28.90	28.64	20.79	3.82	6.63	88.78	1.070	12.31	.....

[1] This phosphate was used in reinforcing the lower grades of mine-run material.
[2] Combined oxides of iron and aluminum.

An inspection of Table 13 will show that samples Nos. 4–F, 4–T, 8–T. 9–T, 10–T, 11–T, 12–T, 13–T, and 16–T are so low in phosphoric acid as to eliminate them as commercial possibilities, unless they are reinforced with higher grade phosphates. But most of these samples (8–T to 13–T, inclusive) were taken from the waste pond of an old phosphate plant and represent the detritus washed out from run-of-mine material in preparing a high-grade rock for the market. It will also be noticed that in most instances where the phosphate content of the samples is low and the silica content high, there is sufficient clay present to admit of adding enough higher grade phosphate rock to obtain the proper silica-lime ratio without substantially reducing the binding qualities of the resultant mixture.

In Table 14 are given the quantities of sand and coke which were added to 100 parts of the better grades of mine-run phosphate to make up charges suitable for furnace treatment. The composition of these briquetted charges is given in the last six columns of this same table. In Table 15 these same data are given for mixtures of two or more samples of mine-run phosphate, and the figures show how many low-grade deposits may be utilized by mixing the material with that from near-by or adjacent deposits of higher grade.

TABLE 14.—*Briquets suitable for furnace treatment formed by mixtures of natural phosphate rock, sand, and coke.*

Sample No.	Briquet mixture SiO_2:CaO=59:41.			Calculated composition of briquet mixture (air-dried).					
	Rock sample.	Sand.	Coke.	SiO_2.	CaO.	P_2O_5.	Fe_2O_3.	Al_2O_3.	Coke.[1]
	Grams.	*Grams.*	*Grams.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
2	100	5.00	14.32	31.67	22.18	17.96	[2]9.87	.....	12.00
1–F	100	14.85	15.65	32.10	22.25	18.10	1.60	6.44	12.00
1–F(2)	100	5.20	14.35	35.79	24.84	18.00	[2]3.29	.....	12.00
3–T	100	10.27	15.05	32.31	22.47	17.60	3.24	5.54	12.00
5–T	100	20.41	16.40	32.80	22.80	17.62	3.00	4.75	12.00
7–T	100	28.91	17.55	32.70	22.59	17.20	3.31	3.78	12.00
14–T	100	20.85	16.47	32.25	22.40	16.54	3.80	5.39	12.00
15–T	100	22.94	16.75	32.35	22.50	17.09	3.42	5.58	12.00
18–T	100	19.64	16.30	32.00	22.23	16.75	3.35	6.18	12.00

[1] The fixed carbon plus ash considered as coke. The coke used in these experiments contains 14.9 per cent of ash. An analysis of this ash showed that the coke in the briquetted mixture adds 0.98 per cent SiO_2, 0.02 per cent CaO, and 0.63 per cent Al_2O_3,Fe_2O_3 to the mix.

[2] Combined oxides of iron and aluminum.

TABLE 15.—*Briquets suitable for furnace treatment formed by mixtures of high-grade and low-grade phosphate rock with coke.*

Sample No.	Briquet mixture SiO_2: CaO=59: 41.			Calculated composition of briquet mixture (air-dried).					
	Rock sample.	Sand.	Coke.	SiO_2.	CaO.	P_2O_5.	Al_2O_3.	Fe_2O_3.	Coke.[1]
	Grams.	*Grams.*	*Grams.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
4–F	44.4	.....	13.63	36.04	24.01	17.69	[2]3.84	.....	12.00
1–F(2)	55.6								
3–T	35.48	.....	13.63	31.42	20.92	17.00	3.80	5.00	12.00
4–T	64.52								
7–T	44.7	.....	13.63	31.50	21.90	16.83	3.74	4.49	12.00
8–T	55.3								
15–T	63.6	.....	13.63	30.80	21.45	16.95	4.25	6.68	12.00
16–T	36.4								
18–T	33.33								
19–T	33.33	23.10	16.79	33.00	22.95	16.55	4.89	6.37	12.00
20–T	33.33								

[1] The fixed carbon plus ash considered as coke. The coke used in these experiments contains 14.9 per cent of ash. An analysis of this ash showed that the coke in the briquetted mixture adds 0.98 per cent SiO_2, 0.02 per cent CaO, and 0.63 per cent Al_2O_3,Fe_2O_3 to the mix.

[2] Al_2O_3,Fe_2O_3.

In several cases it will be noted that the quantity of phosphoric acid in the briquetted charge is from 1 to 1.5 per cent below that in other mixtures. This is due chiefly to the fact that in addition to the lime combined with phosphoric acid a part of this base present in the original phosphate samples was in the form of carbonate and therefore the sand added to take care of the lime in this latter compound reduced the percentage of phosphoric acid in the briquets.

In preparing the samples for briquetting purposes it was found that a Sturtevant hammer mill would grind run-of-mine phosphate, containing as high as 10 per cent of moisture, to 15 mesh without clogging the mill. From a commercial standpoint this is a very important item, since much of the material as it comes from the mines contains a high percentage of moisture, the removal of which would prove quite costly. Moreover, since the presence of from 7 to 10 per cent of moisture in the final mixture is necessary in order to give the material the proper plastic qualities for briquetting purposes, it would be unfortunate to have to dry the phosphate only to wet it again in order to briquet it. Where the material is so dry that it requires the addition of moisture before it can be briquetted, the water can best be added to the sand and coke, with which the phosphate is subsequently mixed. It has been found unnecessary to grind the phosphate finer than that which will go through a sieve having 15 meshes to the linear inch, although finer grinding aids somewhat in imparting greater resisting power to the briquets and probably accelerates slightly the rate of the reactions in the furnace.

The briquetting machine of semicommercial size used in preparing the phosphate charges for furnace treatment is illustrated in Plate II.

In Tables 16 and 17 are given the results of the shatter and compression tests on briquets made from mixtures of relatively high-grade phosphate, sand, and coke, as well as those on briquets made up of mixtures of two or more phosphates. The briquets were made up with varying percentages of moisture and the shatter and compression tests were applied not only to the freshly made briquets but also to the air-dried and oven-dried samples.

TABLE 16.—*Shatter tests on briquets made from natural phosphate rock, sand, and coke.*

Sample No.	Fresh briquets.			Air-dried briquets.[1]			Oven-dried briquets.	
	Weights.	H_2O.	Shattered on dropping to cement floor.	Shattered on dropping to cement floor.	Withstood drop on mass of similar briquets.	Compression test.	Shattered on dropping to cement floor.	Withstood drop on mass of similar briquets.
	Grams.	*Per cent.*	*Feet.*	*Feet.*	*Feet.*	*Pounds per sq. in.*	*Feet.*	*Feet.*
1-F	107.0	11.21	5	4	.....	.....	6	14
1-F	105.5	13.53	10	5	.....	.....	9	16
1-F	108.7	13.45	20+	.....	.....	.....	8	20
2	110.0	10.00	20+	7	.....	.....	.....	.....
3-T	133.5	8.69	4	5	18	472	9	20
3-T	124.7	11.15	8	6	20	800	10	20
3-T	115.2	13.63	14	7	20	838	12	20
5-T	113.7	11.08	8	7	20	483	11	20
5-T	126.4	13.13	12	8	20	654	12	20
7-T	122.1	10.49	.....	5	.....	.....	7	20
7-T	105.2	9.50	8	6	15	815	9	20
7-T	116.4	13.14	10	7	16	950	12	15
14-T	131.3	9.90	9	6	18	724	9	20
14-T	120.9	10.47	12	6	18	793	10	20
15-T	121.7	9.53	6	8	20	407	11	20
15-T	119.2	12.35	20	7	20	894	13	20
15-T	115.7	12.62	12	11	20	538	10	20
18-T	120.6	13.27	20+	8	20	887	13	20

[1] Average weight=109 grams. Average H_2O content=2.95 per cent.

TABLE 17.—*Shatter tests on briquets made from mixtures of low-grade and high-grade phosphate rock with coke.*

Sample No.	Fresh briquets.			Air-dried briquets.			Oven-dried briquets.	
	Weights.	H_2O.	Shattered on dropping to cement floor.	Shattered on dropping to cement floor.	Withstood drop on mass of similar briquets.	Compression test.	Shattered on dropping to cement floor.	Withstood drop on mass of similar briquets.
	Grams.	*Per cent.*	*Feet.*	*Feet.*	*Feet.*	*Pounds per sq. in.*	*Feet.*	*Feet.*
3-T, 4-T	118.5	12.00	12	12	18	728	14	20
7-T, 8-T	113.5	11.90	8	8	20	738	8	20
7-T, 8-T	103.0	14.30	10	10	20	960	10	20
15-T, 16-T	111.6	14.35	20+	10	20	1,004	18	20
18-T, 19-T, 20-T	121.6	11.02	9	8	15	811	11	20

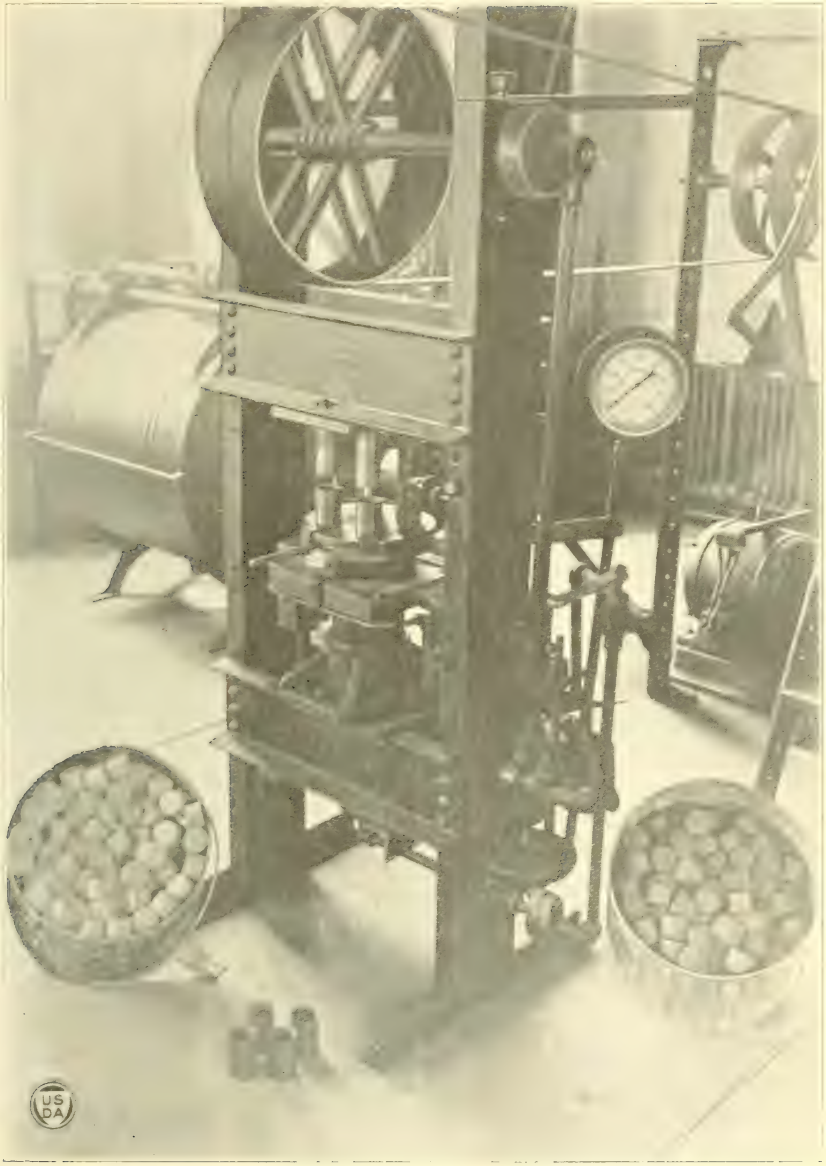
With few exceptions all of the briquets in the air-dried condition withstood a drop on a cement floor of from 6 to 8 feet and a drop of 20 feet or more upon a mass of other briquets. The drying of the briquets in an oven increased somewhat the effectiveness of the binder, but in actual commercial practice it would scarcely be economically feasible to put them through a drying process. In charging these briquets to a shaft furnace, however, they would never be subjected to a drop of over 15 feet upon a mass of similar briquets and therefore they would meet all practical requirements.

Through the courtesy of two commercial firms, briquetted charges of several tons were made up with the silica-lime ratio given in the preceding tables and protracted tests made on a semicommercial scale in a modified form of blast furnace which is described later in this bulletin.

EFFECT OF HIGH TEMPERATURES ON VARIOUS BRIQUETTED MIXTURES.

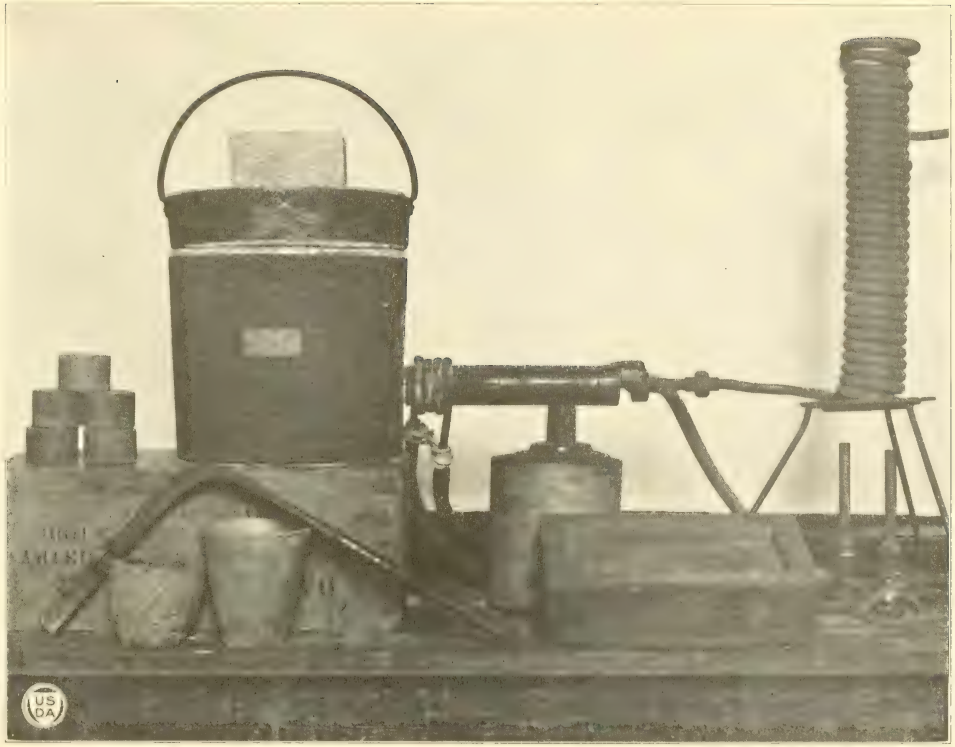
The results obtained in these larger scale experiments indicated that the silica-lime ratio as well as the carbon content of the briquetted charge might be advantageously altered to give a somewhat more rapid evolution of phosphoric acid without sacrificing the fluidity of the slag. Accordingly a series of laboratory experiments was undertaken to determine the following points: (1) The percentage of coke to incorporate in the briquets for optimum reducing effect; (2) the optimum silica content required for the rapid elimination of phosphoric acid and the production of a fluid slag; (3) the most practical temperature to employ to effect the decomposition of the phosphate without undue erosion of the refractory lining of the furnace.

Four batches of briquets were made up of run-of-mine phosphate from Tennessee mixed with sufficient sand to give the following ratios of silica to lime in the charge—59:41, 61:39, 63:37, and 68:32. The amount of coke in the first batch of briquets (having the lowest silica content) varied between 12 and 15 per cent of the weight of the charge, and in certain briquets bituminous coal was substituted



S. 11142.

SMALL BRIQUETTING PRESS USED IN PREPARING PHOSPHATE CHARGE FOR FURNACE TREATMENT.



S. 11630.

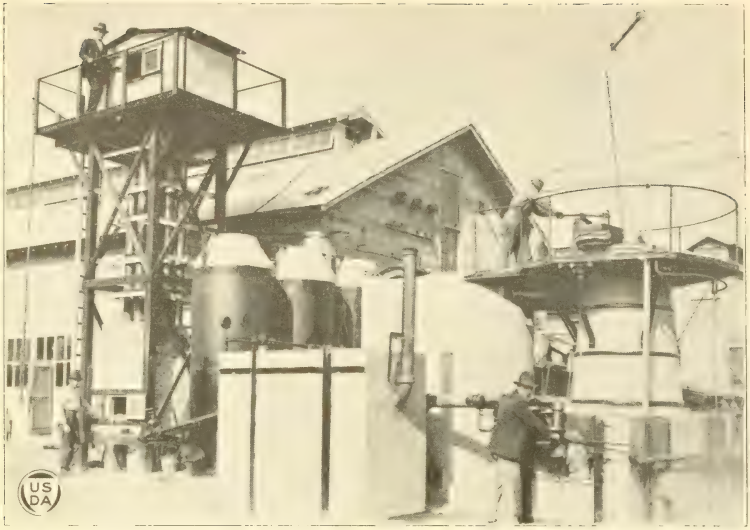
LABORATORY FURNACE USED IN PRELIMINARY EXPERIMENTS WITH BRIQUETTED CHARGES OF MINE-RUN PHOSPHATE, SAND, AND COKE. THE COIL FOR PREHEATING THE AIR IS SHOWN ON THE EXTREME RIGHT AND THE WATER-COOLED BURNER IS SHOWN IN THE CENTER.

S. 10380.

FIG. 1.—SEVERAL TYPES OF BRIQUETS USED IN LARGE-SCALE EXPERIMENTS ON THE VOLATILIZATION OF PHOSPHORIC ACID IN AN OIL-BURNING FURNACE.

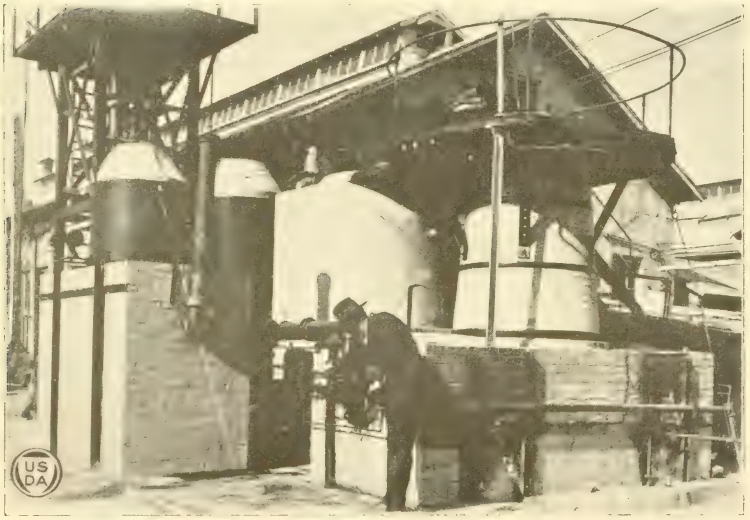
S. 10379.

FIG. 2.—EFFECT OF THE OIL FLAME ON BRIQUETTED CHARGE BEFORE FUSION TAKES PLACE. UNBURNED BRIQUETS ON RIGHT, BURNED BRIQUETS ON LEFT, AND BROKEN BURNED BRIQUETS IN CENTER SHOWING UNALTERED CARBON WITHIN THE MASS.



S. 11476.

FIG. 1.—GENERAL VIEW OF ONE OF THE EARLIER OIL-BURNING FURNACE PLANTS FOR THE VOLATILIZATION OF PHOSPHORIC ACID, ARLINGTON EXPERIMENTAL FARM, VA., SHOWING FURNACE DUST CATCHER, PREHEATER, STOVES, AND ELECTRICAL PRECIPITATOR.



S. 11477.

FIG. 2.—A CLOSER VIEW OF THE FURNACE PROPER SHOWING SLAG HOLES IN CRUCIBLE.

for coke, this coal being added in sufficient quantity to supply 10 per cent of fixed carbon to the mass. After a number of tests, however, it was found that 14 per cent of coke was ample to give the proper reducing reaction and this amount was used in the three other batches of briquets where higher proportions of silica were employed.

In these experiments the same type of small injector gas furnace was used as that employed in the preliminary work where pure mixtures of tricalcium phosphate, silica, and carbon were smelted, but in order to obtain somewhat higher temperatures than previously employed, the air for the combustion of gas was passed through a steel coil heated by two Bunsen burners. The air was thus preheated to a temperature of 250° C. This apparatus is shown in Plate III.

When the furnace had been brought up to a temperature of about 1,575° C. a single briquet was dropped into an open graphite crucible and the heating continued from 20 to 50 minutes, readings being made at intervals of 5 to 10 minutes with an optical pyrometer. Evolution of phosphoric acid usually began about 3 minutes after the introduction of the briquet and at the expiration of 10 minutes the fumes were copiously evolved. The slags produced were poured upon a hollowed-out carborundum brick and after cooling were ground to 80 mesh and the phosphoric acid remaining therein determined by analysis, that which was evolved being calculated by difference. The results of these experiments are shown in detail in Table 18.

TABLE 18.—*Time and temperature required for the volatilization of phosphoric acid from briquetted charges of phosphate rock, sand, and coke containing different ratios of CaO to SiO_2.*

Sample No.	Composition of briquets (exclusive of carbon).					Coke.	Silica-lime ratio, SiO_2: CaO.	Time of fusion.	Temperature.	P_2O_5 in slag.	P_2O_5 volatilized.	Character of slag.
	SiO_2.	CaO.	P_2O_5.	Fe_2O_3.	Al_2O_3.							
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*		*Min.*	*° C.*	*P. ct.*	*P. ct.*	
50, 81	37.9	26.4	18.1	4.1	4.6	14	59:41	20	1,600	4.93	76.4	Liquid ,dark, glassy, translucent, small amount pyrophosphate.
49, 90	37.9	26.4	18.1	4.1	4.6	14	59:41	25	1,595	4.33	79.4	Do.
57, 48	37.9	26.4	18.1	4.1	4.6	12	59:41	30	[1]1,575	6.77	66.8	Liquid, bluish, glassy, slight opalescence, no pyrophosphate.
83	37.9	26.4	18.1	4.1	4.6	15	59:41	30	[1]1,580	4.00	81.0	Liquid, dark, glassy, translucent, small amount pyrophosphate.
75, 83, 88, 101	37.9	26.4	18.1	4.1	4.6	14	59:41	30	1,610	2.65	87.6	Very liquid, light, glassy, translucent, very small amount pyrophosphate.
85, 86	37.9	26.4	18.1	4.1	4.6	14	59:41	35	1,605	1.18	94.6	Very liquid, light, glassy, translucent, no pyrophosphate.
49	37.9	26.4	18.1	4.1	4.6	12	59:41	40	[1]1,590	2.5	88.4	Liquid, light, glassy, translucent, no pyrophosphate.
108, 109	37.9	26.4	18.1	4.1	4.6	14	59:41	40	1,640	1.63	92.5	Very liquid, light, glassy, translucent, no pyrophosphate.
56	37.9	26.4	18.1	4.1	4.6	15	59:41	50	1,590	1.08	95.0	Very liquid, dark, glassy, translucent, no pyrophosphate.
57, 82	37.9	26.4	18.1	4.1	4.6	[2]10	59:41	20	1,570	6.17	70.0	Liquid, black, glassy, translucent, no pyrophosphate.
99	37.9	26.4	18.1	4.1	4.6	[2]10	59:41	25	1,595	3.16	85.1	Liquid, dark, glassy, translucent, no pyrophosphate.
74, 78	37.9	26.4	18.1	4.1	4.6	[2]10	59:41	30	1,615	.57	97.4	Very liquid, light, glassy, translucent, no pyrophosphate.
68, 113	40.0	25.6	17.5	4.0	4.5	14	61:39	20	1,595	6.85	65.0	Liquid, bluish, glassy, slight opalescence, large amount pyrophosphate.
92, 104	40.0	25.6	17.5	4.0	4.5	14	61:39	25	1,585	4.62	77.0	Do.
76, 87	40.0	25.6	17.5	4.0	4.5	14	61:39	30	1,615	1.25	94.1	Liquid, dark, glassy, translucent, no pyrophosphate.
71	40.0	25.6	17.5	4.0	4.5	14	61:39	35	[1]1,610	.11	99.5	Slightly viscous, dark, glassy, slightly crystalline, no pyrophosphate.
70, 79	42.0	24.7	17.0	3.8	4.3	14	63:37	20	1,605	5.81	69.6	Liquid, bluish, glassy, translucent, medium amount pyrophosphate.
93, 94	42.0	24.7	17.0	3.8	4.3	14	63:37	25	1,610	3.12	84.1	Viscous, bluish, glassy, slight opalescence, medium amount pyrophosphate.
67, 77, 84	42.0	24.7	17.0	3.8	4.3	14	63:37	30	1,610	.52	97.4	Viscous, light, glassy, translucent, small amount pyrophosphate.
72	42.0	24.7	17.0	3.8	4.3	14	63:37	35	[1]1,610	.12	99.4	Viscous, dark, glassy, translucent, small amount pyrophosphate.
106	47.8	22.3	15.3	3.5	4.0	14	68:32	20	1,590	4.04	76.5	Viscous, blue, glassy, opalescent, large amount pyrophosphate.
95	47.8	22.3	15.3	3.5	4.0	14	68:32	25	1,585	2.14	87.8	Do.
97, 98	47.8	22.3	15.3	3.5	4.0	14	68:32	30	1,610	.50	97.2	Viscous, bluish, glassy, slight opalescence, medium amount pyrophosphate.
111	47.8	22.3	15.3	3.5	4.0	14	68:32	35	1,640	.22	98.8	Very viscous, dark, glassy, translucent, small amount pyrophosphate.
110	47.8	22.3	15.3	3.5	4.0	14	68:32	40	1,630	.21	98.9	Do.

[1] Estimated temperature.

[2] Coal.

The data given in the above table show that, on the whole, an increase in the silica content of these briquetted mixtures resulted in a more rapid evolution of phosphoric acid, but usually at the sacrifice of the fluidity of the slag.

The ratios of silica to lime in the first and third batches of briquetes—namely, 59 : 41 and 63 : 37—do not correspond to any definite calcium silicates but the proportions of these two ingredients (61 : 39 and 68 : 32) in the second and fourth batches coincide closely to the ratios of silica to lime in calcium trisilicate ($Ca_2Si_3O_8$) and calcium di-meta silicate ($CaSi_2O_5$), respectively.

Where the proportion of silica to lime was 59 : 41 (first batch of briquets) it required from 40 to 50 minutes to drive off the phosphoric acid from the charge at a temperature of 1,600° C. In every other instance, however (where the silica content was higher), the nearly complete volatilization of phosphoric acid was accomplished in from 30 to 35 minutes. Yet the slight increase in the rate of evolution of P_2O_5 where the proportion of silica to lime was raised above that in the second batch of briquets (namely, 61 : 39) was insufficient to offset the disadvantages of having a more viscous slag to tap and a greater weight of charge to smelt. Therefore a charge having the proportion of 61 silica to 39 lime was adopted as the most practical for the subsequent large-scale experiments.[46]

Another important point brought out by these experiments is the possibility of using bituminous coal as a reducing agent in the briquets in lieu of coke. Not only was it found that the evolution of the volatile hydrocarbons which are given off in the preliminary heating of such mixtures did not disintegrate or split the briquets but that there was an actual deposition of carbon (from the decomposition of hydrocarbons) throughout the mass which seemed to aid in the subsequent reduction of the phosphate mineral. These facts open up an interesting line of research on the feasibility of substituting coal for at least part of the coke in the furnace charge. It seems probable, however, that such a procedure would necessitate altering the design of the furnace so that the extra amount of combustible gases evolved could be taken care of before the phosphoric acid was passed into the collector.

The several types of briquets used in this experimental work are shown in Plate IV, Figure 1, and the effect of the preliminary heating on these briquets (before fusion takes place) is shown in Plate IV, Figure 2.

The average temperature obtained in the experiments recorded above was approximately 1,600° C., although at times individual readings showed as high as 1,700° C. Either of these temperatures, however, is below the maximum obtained in blast-furnace practice, and where water-cooling devices are employed no undue erosion of the furnace lining is anticipated. It is true that the acid character of the slag produced in smelting the phosphate charge has a tendency to attack more vigorously a fire-brick lining than the basic or neutral slag obtained in the smelting of iron, but a balance would soon be

[46] In the larger scale experiments subsequently described it was found, however, that the slags produced from charges of this composition congealed so readily that the tapping of the furnace was often rendered somewhat difficult. Further experimental work is being conducted with a view to determining a charge composition which will give a slag of greater fluidity at lower temperatures than 1,600° C. without materially reducing the evolution of P_2O_5.

established where the slag would freeze upon the furnace walls, protecting them from further action by the molten charge.

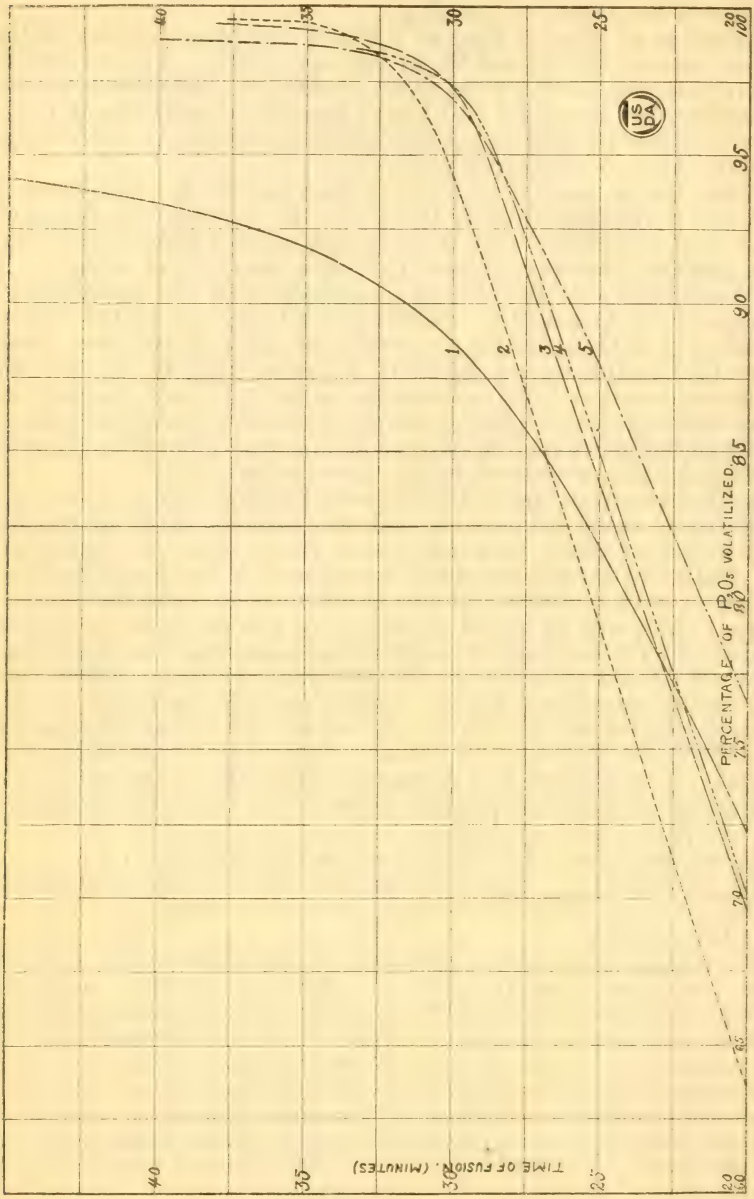


FIG. 11.—Curves showing rate of volatilization (at 1,600° C.) of phosphoric acid from briquetted mixtures of phosphate rock, sand, and coke (or coal) having various silica-lime ratios. Curve No. 1, silica-lime 59:41; Curve No. 2, silica-lime 61:39; Curve No. 3, silica-lime 63:37; Curve No. 4, silica-lime 59:41 (bituminous coal); Curve No. 5, silica-lime 68:32.

In the above chart (fig. 11) the rate of volatilization of P_2O_5 from briquets of various compositions is graphically illustrated by curves.

LARGER SCALE EXPERIMENTS.

With the exception of a few experiments conducted in the furnace shown in Figure 9, *A*, practically all of the larger scale work on the volatilization of phosphoric acid from briquetted charges of phosphate rock, sand, and coke have been conducted in furnaces having certain features of both the open-hearth and blast-furnace types. While the dimensions of the furnace proper, the materials used for linings, and the character of the outer shell have been altered from time to time, the present furnace plan is in a general way the same as that employed in the earlier experiments. Briefly, this furnace consists of an elongated arched crucible, 12 feet in length, 2 feet in diameter, and 2 feet in height at the crown of the arch. In the center of the arched roof of this chamber is a circular opening leading up into a shaft or charge chamber 7 feet 6 inches in height and having the shape of the usual type of blast furnace. The throat of the chamber where it discharges onto the furnace hearth was originally 12 inches in diameter, but this was later reduced to 10 inches. This charge chamber widens out gradually until at the top of the bosh the internal diameter is 2 feet. From here on the walls of the chamber taper inwardly until at the top of the shaft the opening is only 14 inches in diameter. This chamber holds approximately 700 pounds of briquetted charge. One foot from the top of the furnace shaft is a flue leading into a dust chamber. The furnace was originally constructed entirely of fire brick, but after a number of experiments it was found that the temperatures attained were so high (1,500° to 1,700° C.) that it was desirable to replace them in part by carborundum brick, particularly since in the earlier work neither the crucible nor furnace shaft were steel jacketed and therefore no water-cooling devices could be employed.

Both the dust catcher and the stoves for burning any combustible gases evolved from the furnace and regenerating the heat in the effluent gases were originally constructed of fire brick without any outer steel casing. These stoves were built together with a view to reducing radiation losses, but this plan also was found to be impractical, since it was impossible to render the common walls of these stoves sufficiently tight to prevent the gases from one stove mixing with the air passing through the adjoining one. The likelihood of thus causing an explosion made it necessary to abandon them as a means for heating the air to the oil burners, so they were used only to burn the combustible gases evolved from the furnace. In order to obtain the preheated air which should have been furnished by the stoves, a fire-brick chamber was built containing a coil of 60 feet of 4-inch steel pipe heated by means of a small oil burner. The air required for the furnace in these earlier experiments was furnished by three Leiman positive-pressure blowers, two having a capacity of 160 cubic feet of free air per minute each and the third a capacity of 360 cubic feet. When the furnace was well heated the large and one small blower were employed to supply the air. These discharged into a 4-inch main which was constricted at each burner to 3 inches in diameter. Views of the furnace plant used in this earlier work are shown in Plate V, Figures 1 and 2.

The oil burners finally adopted for the furnace and the ones which are still being employed operate with high-pressure oil (from 50 to 200 pounds per square inch) but with air at relatively low pressure

(4 to 8 ounces). The consumption of oil by these burners is controlled by the pressure and also by the size of the openings in the tips used. These burners work exceedingly well as long as the oil fed to them is thoroughly strained, but clog very readily if all sediment is not completely removed. The ends of these burners are surrounded by steel water jackets which in turn are set into the ends of the furnace at an angle of about 60° from the horizontal, so that the oil flame plays directly upon the hearth. A steel tank holding 500 gallons is used as the main reservoir for the fuel oil, this tank being connected with a small 80-gallon tank provided with a gauge to measure the oil consumption. The oil is fed by gravity to a pump which forces it to the burners under a pressure of from 30 to 200 pounds per square inch.

The phosphate used in the experiments with this first equipment was from hard-rock phosphate mines near Newberry, Fla. This material was run-of-mine phosphate, containing sufficient natural binder to make a good grade of briquets, which stood up well under preliminary shatter tests and exhibited no tendency to disintegrate upon being suddenly heated to a high temperature. The phosphoric acid content of this briquetted charge, exclusive of moisture and carbon (both of which are finally eliminated), was 19.99 per cent.

A number of tests were made in this furnace before the auxiliary equipment was changed and the results of the last two experiments have already been described in detail,[47] but brief summaries are given below.

The first of these latter tests was conducted for a period of only 10 hours, during which time 2,200 pounds of briquetted charge were smelted. The rapid rate, however, at which this material melted in the shaft and discharged onto the furnace hearth allowed the lower strata of slag to cool to the point where phosphoric acid was not readily evolved, and also resulted (toward the latter part of the run) in the material freezing in the cinder notches, so that the furnace could not be tapped and had to be closed down. The average temperature of the preheated air delivered to the oil burners during the greater part of this run was 250° C. and the highest temperature recorded on the hearth was 1,500° C. The volatilization of phosphoric acid ranged between 38 and 63.5 per cent, or an average of 52 per cent, the rate of evolution being about 80.5 pounds P_2O_5 per hour. Since the oil consumption toward the last of the test was 9½ gallons per hour, the yield (figured on this basis) was approximately 8.5 pounds of P_2O_5 per gallon of fuel oil.

The next test was continued for a period of 20 hours, during which time 3,500 pounds of briquetted charge were smelted and run out of the furnace in a molten condition. In the earlier stages of this run numerous mechanical difficulties were encountered, but in the last 3½ hours of the test the furnace appeared to operate quite efficiently and an average volatilization of 97 per cent P_2O_5 was obtained. The preheated air was delivered to the burners at temperatures ranging from 325° to 350° C. and the hearth temperature was between 1,500° and 1,600° C. The final slag tapped had an average content of 0.77 per cent P_2O_5, which corresponds to a volatilization of 97 per cent of that present in the original charge. The rate of evolution was 46.3

[47] Investigations on Pyrolytic Production of Phosphoric Acid. Jour. Chem. and Met. Eng. 23, p. 1057 (1920).

pounds per hour. The oil consumption toward the last of the test was reduced to 8.3 gallons per hour, yet the temperature of the furnace seemed to be efficiently maintained, so on this basis a volatilization of 5.6 pounds of P_2O_5 per gallon of fuel oil was obtained. The old electrical treater (previously described) was used in this test, and since the precipitator pipes not only had too small a capacity but were also badly out of line, only a small proportion of the acid evolved was collected. The concentration of this acid varied from 21.5 per cent to 64 per cent H_3PO_4, the stronger acid being collected toward the last of the run, when the temperature of the system had risen to the point where much less moisture condensed.

PRESENT FURNACE EQUIPMENT AND LATEST RESULTS.

After the completion of the experiments just described it was found that the fire-brick linings of the shaft and in the central portion of the crucible arch were in such bad condition that it was desirable to rebuild the furnace. In this later furnace the crucible and lower part of the furnace shaft were lined entirely with carborundum brick, fire brick being used only in the outer layers of the furnace walls and in the upper part of the charge chamber (above the bosh). The old stoves (having a common wall) were also torn down and replaced by four individual steel shells 4 feet in diameter and 10 feet high. Each of these shells was lined with fire brick and divided into two chambers—one for burning the combustible gases and the other filled with checker brick to act as a heat reservoir for preheating the air delivered to the oil burners. Suitable inlets and outlets (controlled by valves) were provided for the air and gas. An exhaust fan placed between the stoves and the electric precipitator served to draw the gases from the furnace through the stoves and introduce them into the collector, the temperature of these gases being reduced when necessary by a cooler surrounding the gas main. A "Roots" positive-pressure blower capable of delivery of 1,000 cubic feet of free air per minute under a maximum pressure of 4 pounds per square inch replaced the three small blowers previously used, and the air main to the oil burners was increased from 4 inches to 6 inches in diameter. There were also installed a recording gauge to show this air pressure and an instrument (Tapalog) connected with two pyrometers, which recorded the temperature of the gases from the stoves to the precipitator and that of the air delivered to the burners.

By means of a small pipe (a bleeder) inserted in the furnace flue samples of the gases were withdrawn from time to time and analyzed. After considerable experimentation with this equipment the old fire-brick dust catcher also was removed and a steel cylinder lined with fire brick and provided with two baffle walls was used in its place.

A number of experiments lasting from 10 to 20 hours were conducted in this furnace, but it became evident that water-cooling devices must be employed in order to maintain unaltered the interior dimensions of the furnace shaft, since in protracted tests the combined effects of the high temperature and the erosive action of the slag gradually wore away the linings. Accordingly the furnace shaft was again torn down and replaced by a steel shell lined in the lower portion with carborundum brick and in the upper portion with fire brick. This shell was bolted to a bronze basin which fitted over the carbo-

rundum arch of the furnace crucible. A water curtain was caused to flow over this shaft by means of a perforated pipe coiled around the upper part of the steel shell, this water being caught in the bronze basin mentioned above, from which it flowed by gravity to a steel tank holding 7,000 gallons and was returned to the furnace by a circulating pump. Individual steel plates (without any water-cooling devices) were bolted to the sides and ends of the crucible, it having been learned from previous experience that only the center of the crucible arch was appreciably affected by the temperatures attained.

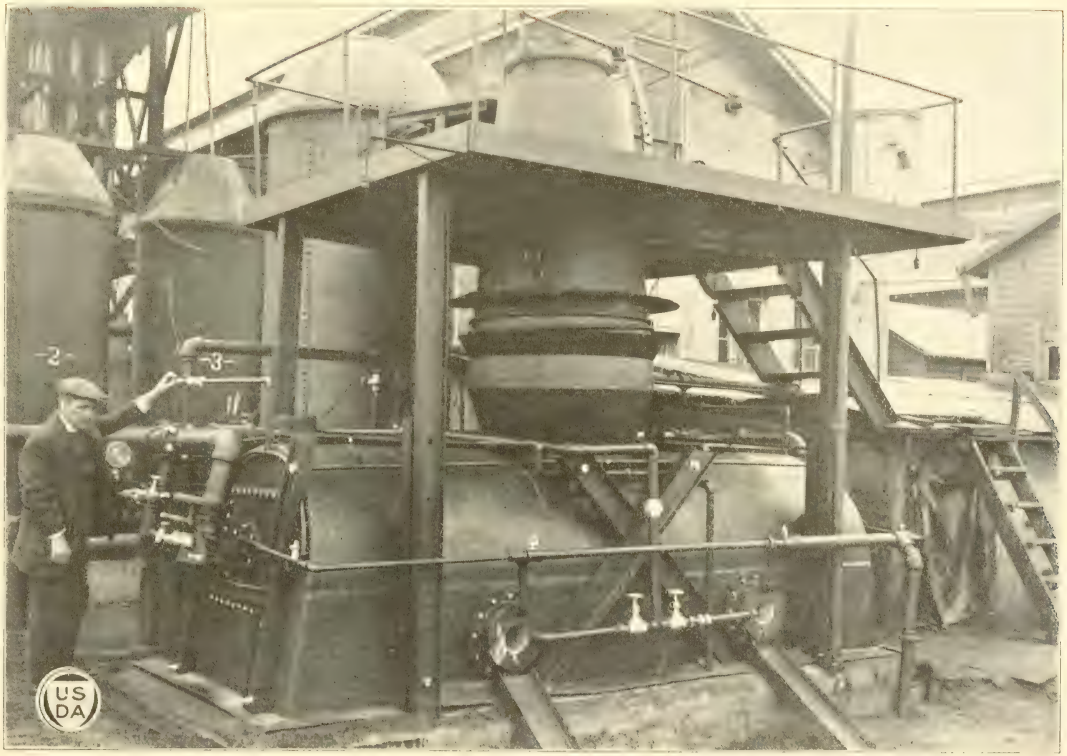
The first of the tests described below was made with this modified furnace, but while the water-cooled shaft and bronze basin answered the purpose for which they were intended admirably, leakage of the flame and gases through the joints of the crucible caused overheating and buckling of the steel plates, a condition which grew worse as the run continued. Considerable difficulty was also caused by the breaking through of the slag at the tap holes, which made it apparent that it was not only necessary to have a gas-tight crucible but water-cooled cinder notches as well. While this test was only continued efficiently for five and a half hours after the furnace was first charged, a brief summary of the operation is given below.

During the period between 2.40 and 5.15 p. m. July 26, 1922, 1,175 pounds of briquets having a phosphoric acid content of 15.65 per cent were charged to the furnace, this being largely tapped off at 5.40 p. m. The oil pressure during this period was maintained at 45 pounds, equivalent to a consumption of 17 gallons per hour, and the temperature of the preheated air delivered by the stoves to the oil burners was 135° C. The average phosphoric acid content of this slag was 0.72 per cent, which is equivalent to a volatilization of 96.7 per cent, or 3.5 pounds per gallon of fuel oil consumed. This evolution was surprisingly high in view of the fact that the temperature recorded on the hearth at the time of tapping was only 1,470° C. While this slag was being run off, 200 pounds more of briquets were added, but unfortunately almost immediately after the furnace was tapped an explosion occurred which blew off the top of one of the stoves, thus entailing a shutdown for a considerable period and a cooling of the furnace. Between 6 and 9.30 p. m. the furnace was only operated spasmodically, but during this time 450 pounds of briquetted charge were added. Much of this froze in the shaft, causing a stoppage of the draft and rendering it impossible to melt this charge out of the shaft with the oil flame, although attempts were made to dislodge it until 2.30 the following morning, at which time the burners were cut off and the furnace closed down.

Before the last test described below was undertaken a steel shell varying in thickness from one-fourth to three-eighths inch was fitted around the furnace crucible, the joints being acetylene welded and the junction between the shell and the bronze basin braized. This change rendered the crucible and shaft of furnace gas tight. Water-cooled cinder notches of cast iron were inserted in the slag holes and bolted to the steel jacket. A system of perforated pipes made it possible to run a water curtain over the entire furnace shell. This water ran into a 6-inch steel trough riveted to the base of the furnace jacket and from here flowed into the large tank previously mentioned, from which it was returned to the system. From the standpoint of durability this furnace has proven eminently satisfactory, as after the last experimental run, lasting 70 hours, during

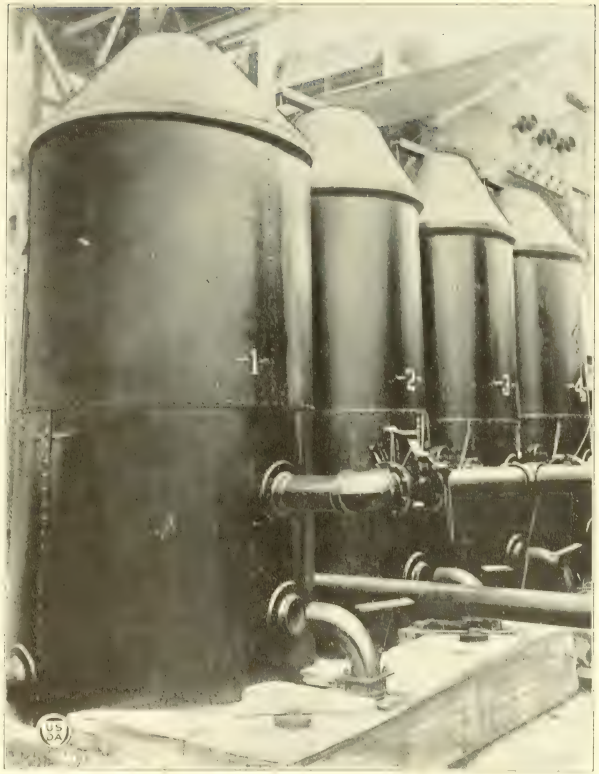
S. 11625.

GENERAL VIEW OF THE LATEST EXPERIMENTAL PLANT FOR THE VOLATILIZATION OF PHOSPHORIC ACID. ARLINGTON EXPERIMENTAL FARM, VA. PICTURE TAKEN JUST AFTER AN EXPERIMENTAL RUN OF 70 HOURS.



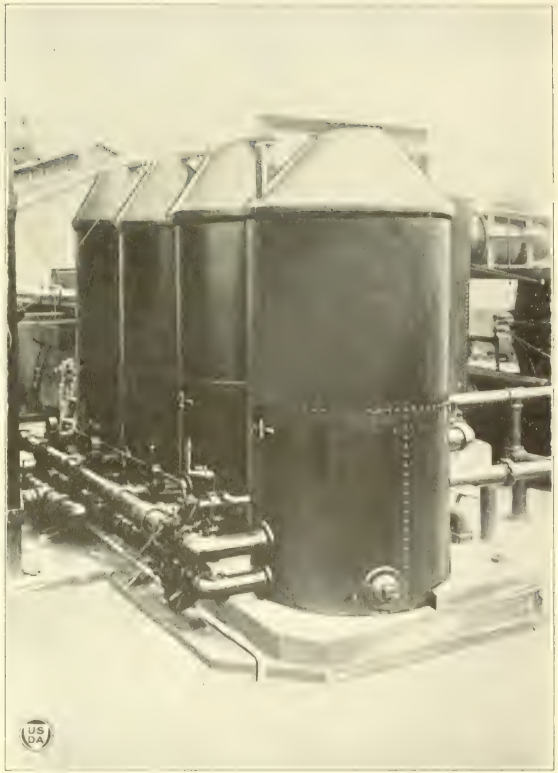
S. 11627.

A Close View of the Latest Type of Furnace Used in Smelting Briquetted Charges of Mine-run Phosphate and Volatilizing the Phosphoric Acid Therefrom. The Furnace Proper, Cinder Notches, and the Oil Burners Are All Water Cooled.



S. 11416.

FIG. 1.—VIEW OF STOVES USED IN CONNECTION WITH PRESENT EXPERIMENTAL PLANT. SLIDING VALVES (BELOW) FOR HANDLING GAS FROM FURNACE. AIR MAIN (ABOVE) FOR DELIVERING PREHEATED AIR TO OIL BURNERS.



S. 11415

FIG. 2. VIEW OF OPPOSITE SIDE OF STOVES. COLD AIR MAIN (ABOVE) HOT GAS MAIN (BELOW) CARRYING P.O. TO ELECTRICAL TREATER.

S. 11631.

FIG. 1.—COTTRELL PRECIPITATOR OR TREATER FOR THE COLLECTION OF VOLATILIZED PHOSPHORIC ACID. PICTURE TAKEN BEFORE ELECTRIC CURRENT HAD BEEN THROWN ON. NOTE THE COPIOUS FUMES OF P_2O_5 BEING EVOLVED.

S. 11629.

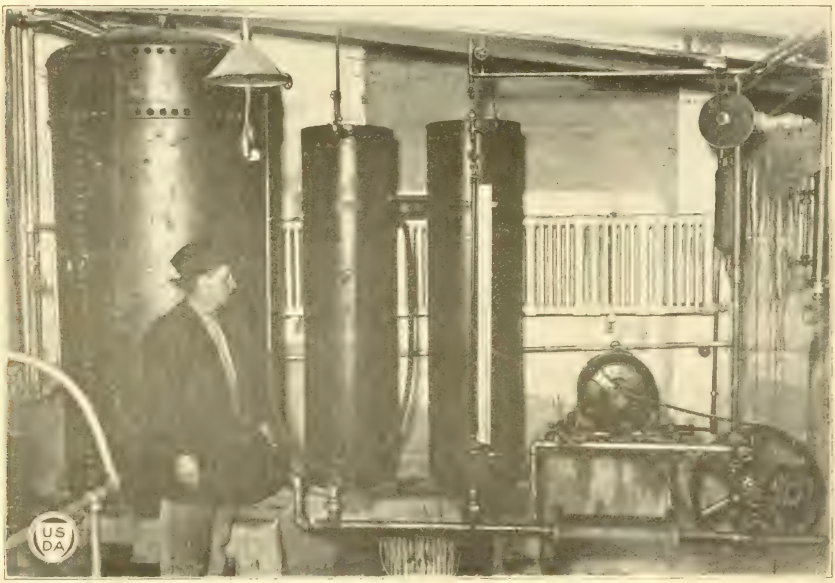
FIG. 2. PICTURE TAKEN TWO MINUTES LATER WITH ELECTRIC CURRENT ON AND FUMES OF P_2O_5 BEING COLLECTED.

S. 9524.

MOTOR GENERATOR SET AND MECHANICAL RECTIFIER USED IN CONNECTION WITH ELECTRICAL PRECIPITATOR.

S. 11628.

FIG. 1.—POSITIVE PRESSURE BLOWER FURNISHING AIR TO THE OIL BURNERS USED IN CONNECTION WITH THE LATEST PHOSPHORIC ACID FURNACE AT ARLINGTON EXPERIMENTAL FARM, VA.



S. 11632.

FIG. 2.—VIEW OF OIL TANKS AND PUMPING EQUIPMENT, WHICH DELIVERS THE FUEL OIL TO THE FURNACE AT A PRESSURE OF FROM 30 TO 100 POUNDS PER SQUARE INCH. THE AMOUNT OF OIL CONSUMED WITHIN A GIVEN PERIOD IS MEASURED BY THE GAUGE SHOWN ON ONE OF THE SMALLER TANKS.

which time over 4 tons of charge were smelted and tapped off as a molten slag, it is in excellent condition and ready for further experimentation.

Views of this latest plant are shown in Plates VI to XI, inclusive, and a plan view of the entire equipment is given in Figure 12.

The data obtained in this three-day test, however, were not very satisfactory, owing to certain mechanical difficulties encoun-

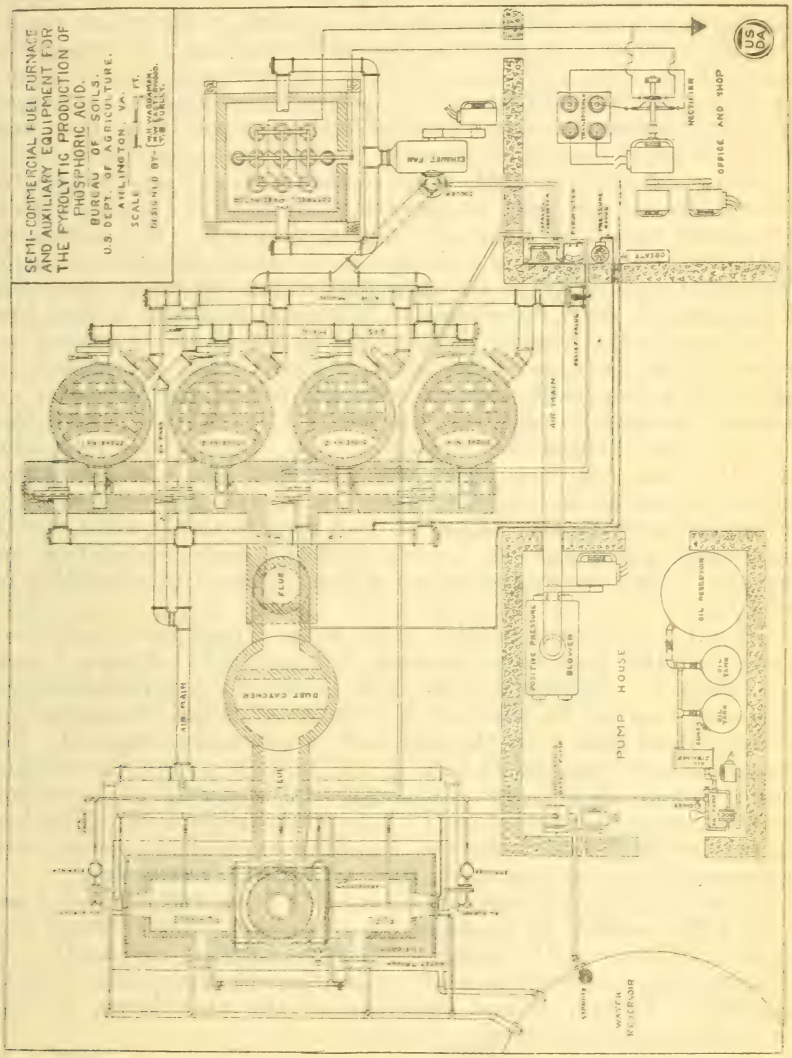


FIG. 12.—Plan of experimental plant.

tered throughout the run and the poor quality of the fuel oil which was furnished. It is felt, therefore, that no fair approximation of the proportion of fuel oil required to the amount of charge smelted can be made.

The oil burners were started at 8.30 a. m., November 8, 1922, after a coke fire had been burning in the furnace shaft for several days. The cinder notches were closed and the first briquets added at

2.50 p. m. Between this time and 5 p. m. 1,600 pounds of charge were added. The temperature of the gases to the stoves had at this time risen to 600° C., but the temperature of these regenerators was only sufficient to heat the air delivered to the burners to 75° C. During much of this time an oil pressure of 70 to 80 pounds was maintained which was equivalent to a consumption of between 25 and 27 gallons per hour, but this pressure was reduced to 45 pounds or 20 gallons per hour [48] at 6 p. m. The furnace was tapped for the first time at 7.10 p.m., the slag obtained being rather viscous and with a tendency to freeze in the cinder notches. This slag contained 8.05 per cent P_2O_5, equivalent to an evolution of only 61 per cent, or a yield of 1.83 pounds P_2O_5 per gallon of fuel oil consumed.

The cinder notches were closed at 7.45 p. m. and from then until midnight a great deal of mechanical trouble was encountered, owing to the frequent blowing of the fuses of the motor driving the positive-pressure blower, and also to the fact that the oil burners became clogged and would not properly atomize the fuel. The distillation of unburned oil through the charge in the shaft deposited so much carbon in the precipitator that this part of the equipment had to be cut out until it could be cleaned. Moreover, scaffolds formed from time to time in the furnace shaft, owing to the alternate cooling and heating of this portion of the furnace, which made it necessary to operate for considerable periods with the top of the furnace open. Between the time of the last tap and 11.30 p. m., 1,325 pounds of briquets were charged, but owing to the irregularities mentioned above this was not in a very fluid condition and was not tapped completely out of the furnace until 8 a. m. the following morning (November 9), when the temperature of the hearth showed 1,600° C. The average phosphoric acid content of this slag (second tap) was 8 per cent, which is equivalent to a volatilization of only 61.3 per cent P_2O_5.

At 8 a. m. the cinder notches were again closed and the furnace recharged, 1,100 pounds of briquets being added between 9 a. m. and 12.20 p. m. During the first three hours of this period, however, the blower had to be shut off a number of times because of the burning out of fuses, but this difficulty was finally remedied. The furnace was again tapped at 12.30 p. m. (third tap), but this slag had a content of 10.85 per cent P_2O_5, equivalent to only 45.8 per cent volatilization or 1.09 pounds of P_2O_5 per gallon of fuel oil. This high P_2O_5 content in the slag reflected the adverse conditions under which the furnace had been operating for the previous four hours.

The cinder notches were again closed at 1 p. m. and between 1 and 4 p. m. 1,050 pounds of briquets were charged. The average temperature of the air to the burners during this period was 200° C. At 3.15 p. m. a gas analysis was made which showed practically complete combustion of the fuel and oxidation of the phosphorus evolved. This analysis is given below:

	Per cent.
PH_3	1.0
CO_2	13.2
O_2	.4
CO	2.8
N_2	82.6

[48] On account of the clogging of the burner tips from time to time, a definite oil pressure did not always deliver the same quantity of oil per hour.

The furnace was again tapped at 4.30 p. m. and this slag (fourth tap) showed 12.78 per cent of P_2O_5 or a volatilization of 34.9 per cent. Since the temperature of the hearth on tapping was 1,570° C. and the working conditions apparently rather good during the period, the high P_2O_5 content of this slag is somewhat difficult to explain. It was probably due, however, to rapid charging immediately after tapping the previous slag when operating conditions had been so adverse, and also to the fact that the oil consumption was so high that the material melted out of the furnace shaft at a more rapid rate than was desirable for the efficient elimination of P_2O_5.

While this fourth tap was in progress 500 pounds of briquetted charge were added and at 6 p. m. the cinder notches were again closed. Between 5 and 8.30 p. m. 1,350 pounds of briquets were charged, but some trouble was experienced during this period, owing to scaffolding in the shaft from time to time. At 9.20 p. m. one side of the furnace was tapped (fifth tap), a portion of the slag showing 5.9 per cent P_2O_5 or a volatilization of 70.1, but another sample of somewhat better appearing slag showed a content of only 1.18 per cent P_2O_5, equivalent to a volatilization of 94.4 per cent. The slag in the north end of the crucible, however, was so viscous that it did not tap readily, a condition which was probably caused by a channel which opened up in the shaft toward this end of the furnace sometime previously, which allowed the combustion of the oil to take place well up in the shaft rather than upon the hearth, where the maximum temperature is desired. One hundred pounds of charge were added between 10.20 and 11.20 p. m., largely to close the channel mentioned above, but the north end of the crucible was not entirely tapped free of slag until 5.45 the following morning. The average phosphoric acid content of this slag (sixth tap) was 7.56 per cent, equivalent to a volatilization of 61.9 per cent P_2O_5. During all of this period the precipitator was cut off for fear the unburned oil or carbonaceous matter which distilled over from time to time would cause deposition of carbon in the precipitator pipes and on the central wires and result in the arcing across of the high-tension current.

When the furnace was freed from the slag of the previous charge and the temperature of the hearth apparently sufficiently high for ready volatilization of P_2O_5 it was decided to put in a charge and allow it to run through and maintain it in a molten condition on the hearth until the evolution of P_2O_5 was no longer apparent. Accordingly between the hours of 7 and 9 a. m. 1,100 pounds of briquets were charged to the furnace. This was melted and ran entirely through the shaft at 10.30 a. m., the top of the furnace being left open during this period in order to observe the fumes. This procedure, of course, resulted in enormous losses of heat energy, not only due to the fact that the gases of combustion were discharged directly into the atmosphere, and therefore no regenerative effect gained as is the case when the shaft is full of charge, but also because the stoves could not be operated under these conditions, and therefore practically no preheated air was employed. During this period from 8 a. m. to 12 noon the oil pressure was maintained at about 75 pounds per square inch, with an average oil consumption of 20 gallons per hour. Fumes of P_2O_5 could no longer be readily detected at noon and at 12.45 p. m. the furnace was tapped. The south cinder notch was opened and a molten slag ran out readily for 15 or 20 minutes (sev-

enth tap), but at the end of this time it was observed that the slag was growing more viscous and upon examination it was found that the oil burners were clogged and no longer properly atomizing the fuel. These burners were therefore removed and the small strainers contained therein found to be almost entirely stopped by some sediment. This shutdown entailed considerable loss of temperature which was not regained until 3.45 p. m., when the cinder notches were again opened and the furnace tapped freely. The average P_2O_5 content of this slag (seventh and eighth tap) was 4.24 per cent, showing a volatilization of 79.4 per cent. Taking the seventh tap (namely, that made at 12.15 p. m.) as indicative of what would have been obtained had the burners not become clogged[49] the evolution of P_2O_5 appears fairly efficient. While the actual figures show a yield of only 1.16 pounds of P_2O_5 per gallon of fuel oil, the conditions under which the furnace was being operated (namely, an empty shaft, no heat regenerative effect, and a relatively high oil pressure) were such that fully three-fourths of the heat value of the oil was lost during the last two hours of operation.

At 5 p. m. the furnace was again charged with a relatively small amount of coke and 550 pounds of briquets. This charge, however, went through to the hearth almost immediately so at 9.30 it was tapped and this slag (ninth tap) showed a P_2O_5 content of 4.4 per cent or a volatilization of 78.5 per cent. At 10 p. m. the furnace was recharged with 150 pounds of coke upon which between the hours of 10 and 11 p. m. 700 pounds of briquets were charged. Batches of 100 pounds were continued at 10-minute intervals up until 11.40 p. m., when a total of 1,000 pounds had been added. At this time the furnace scaffolded somewhat, which was followed by channeling, and the oil pressure was accordingly reduced to 50 pounds. At midnight this pressure was taken down to 40 pounds (a consumption of 15 gallons per hour), since it was apparent that the amount of oil which was being delivered was in excess of that which could be efficiently burned in the furnace crucible. The top of the furnace had to be opened from time to time, since the furnace shaft was emptied at about midnight and this caused the flames to play directly on the furnace top, overheating it at times and also causing the stove valves to become dangerously hot. This heat was continued, the oil pressure being maintained at 40 pounds for the rest of the run. The tapping was begun at 2 a. m., the stoves only being changed once between 10.30 p. m. and 2.30 a. m. and therefore the temperature of the air to burners during this period was less than 75° C. The introduction of a fresh stove at 2.30, however, raised this temperature to 175° C. The furnace was tapped clean, and closed down at 6 a. m. This slag (tenth tap) showed a P_2O_5 content of 4.89 per cent, or a volatilization of 76 per cent P_2O_5, giving a yield of 1.29 pounds of P_2O_5 per gallon of fuel oil. Since the top of the furnace was open, however, a large part of the time before the furnace was tapped, the bulk of the heat energy of the oil was lost. Only a portion of the P_2O_5 was transmitted to the electrical precipitator, but approximately 8 gallons of 45 per cent phosphoric acid was collected toward the last of this run.

[49] While the seventh and eighth taps were analyzed together, the character of the seventh tap indicated a high voltilization of P_2O_5

DISCUSSION OF EXPERIMENTAL RESULTS.

The results of the tests so far conducted with the semicommercial equipment at Arlington Experimental Farm, Va., have demonstrated conclusively that it is feasible to drive off phosphoric acid nearly completely from briquetted charges of phosphate rock, sand, and coke in large-scale operations by means of burning fuel.

It has also been shown that by the use of high-grade refractories and proper water-cooling devices a furnace can be constructed which will withstand the combined effects of extremely siliceous slags and the high temperatures (1,500° to 1,650° C.) attained in this process.

Other points brought out by these experiments are the feasibility and advantages of having auxiliary equipment for heat regeneration and to make sure that only oxidized products are transmitted to the electrical precipitator where the phosphoric acid is collected.

In the present furnace, however, which has a relatively short shaft or charge chamber, it is necessary to localize or concentrate the highest temperature upon the furnace hearth. During the last protracted test (of 70 hours) just described, the impurities present in the oil frequently made it necessary to operate the burners at a rather high pressure in order to obtain proper atomization of the fuel. This high pressure caused a greater fuel consumption than was either essential or desirable, since it resulted in a long flame which burned well up in the shaft, causing the entire charge to soften and settle down upon the hearth in a semifluid condition. The lower levels of this viscous slag, therefore, were not exposed to the maximum temperature for a sufficient time to drive off the phosphoric acid either rapidly or completely. In a furnace of larger dimensions with a higher shaft, and where much greater air pressures are employed (such as in the ordinary blast furnace), trouble of this kind would hardly be encountered, since the charge is kept in a more or less floating condition,[50] and therefore while descending through the shaft is exposed to the necessary high temperatures for a considerably longer period than is possible in a plant of the present size.

The concentration of the heat in the crucible of this small furnace, however, may be accomplished by a more thorough atomization of the oil at the lower pressures, which will result in shorter flames and less fuel consumption. These conditions were apparently fulfilled in some of the other experimental runs where rapid evolution and excellent yields of P_2O_5 were obtained.

For the efficient working of this furnace it is also essential to eliminate the rather frequent shutdowns, such as were necessitated by the failure of the blowing equipment. The ratio of surface area to the volume of this furnace is such that radiation losses are far more serious than in a plant of large capacity. Even fluctuations in the amount of air delivered are apt to cause the formation of scaffolds in the shaft which further upset the relation between the oil and the air required for its combustion. Because of the small diameter of the furnace shaft, a scaffold often means a complete bridging over of the charge, which puts an added load on the blower to force the air through this partially fused mass. While scaffolds also form at times in large blast furnaces, the complete bridging over of the charge

[50] Johnson, J. E., jr. Principles, Operation, and Products of the Blast Furnace, p. 115–122 (1918).

seldom occurs in normal operation, and if so may often be remedied by a momentary reduction in the air pressure.[51]

In order to remedy the main difficulties encountered in the last experimental run of the furnace, arrangements have been made for the installation of a coil of pipe in the oil line to the burners. This coil will be immersed in a vessel which is kept constantly supplied with hot water from the furnace-cooling devices. Such a scheme should make it possible to deliver the oil to the furnace almost at its flash point and thus insure its thorough atomization and immediate combustion.

A variable speed motor for driving the positive-pressure blower will also be installed, which will make it feasible to determine accurately the amount of air being delivered to the furnace, and thus adjust the oil accordingly.

While it is expected that the above changes will largely remedy the mechanical difficulties heretofore experienced, it would be of considerable advantage to substitute a single large pipe stove in place of the four checker brick stoves now employed. In a pipe stove the air for the combustion of the fuel is passed through a series of pipes contained in a casing or chamber lined with fire brick and heated by the hot and burning gases from the furnace. Such an arrangement makes it possible to obtain air at a more constant and uniform temperature and obviates the necessity of shifting stoves. To shift these stoves quickly in the present plant requires two laborers and an experienced man to direct them, and since the scientific personnel available for the protracted runs of this furnace is very limited, every possible device should be employed for conserving the time and energies of those directing the work and collecting the necessary data. An investigation is now being conducted in these laboratories on the effect of mixtures of P_2O_5, water vapor, and other gases at high temperatures on the various metals from which the pipes of such stoves may be constructed.

ESTIMATED COST OF PRODUCTION.

Before data can be obtained which will show conclusively the commercial feasibility of producing phosphoric acid by this process, it will be necessary to eliminate certain of the mechanical difficulties which have so far interfered with the efficient working of the present plant during the more protracted tests. It is believed that these mechanical troubles can be overcome and that then a continuous run of several days will make it possible to obtain figures which will more nearly show the relation between the fuel consumed and the acid eliminated from the briquetted charge. While these figures will be much less favorable in a small furnace than in one of larger dimensions where heat losses through radiation are less serious, if the data so obtained show economies over the sulphuric acid process, even greater economies may be assumed where a plant of commercial size is employed.

During the tests just described, however, there were periods of from three to five hours when the furnace appeared to operate quite efficiently and if the data taken at such times are considered indicative of normal working conditions, the cost of producing phosphoric acid

[51] Johnson, J. E., jr. The Principles, Operation, and Products of the Blast Furnace, p. 348–349 (1918): Wilcox, F. H. Bul. 130, Bureau of Mines, p. 188, 250–252 (1917).

by this method appears economically superior to that which is now almost universally employed.

Probably, if all the factors are considered, the fairest and at the same time some of the most favorable figures showing the ratio of oil consumed to the yield of product were obtained during the latter part of the 20-hour test begun on October 8, 1920. The cost data given below therefore are largely based on these results, and while it is assumed that the operation be conducted on a larger scale, in a furnace with an average daily output of 30 tons of P_2O_5, the fuel consumption per ton of P_2O_5 produced is that actually determined in the last three and a half hours of this test with the Arlington furnace. In Table 19 is given the estimated cost of mine-run phosphate briquetted and ready for furnace treatment, in Table 20 the cost of producing 1 ton (2,000 pounds) of P_2O_5 from this briquetted charge is shown, and in Table 21 the cost of manufacturing available phosphoric acid by treating high-grade washed phosphoric rock with the liquid phosphoric acid thus produced is given.

TABLE 19.—*Quantities and estimated cost of mine-run phosphate and coke braize required per ton of P_2O_5, and cost of briquetting this mixture for furnace treatment.*

Charge and its manipulation for furnace treatment.	Quantity.	Cost—	
		Per ton of material.	Per ton of P_2O_5.
	Pounds.		
Mine-run phosphate and sand	10,542		
Mining	10,542	$0.75	$3.53
Drying	10,542	.25	1.18
Grinding		.25	1.18
Coke braize	1,716	5.00	4.29
Grinding	1,716	.50	.40
Mixing and briquetting	12,258	1.25	7.66
Total		8.00	18.24

TABLE 20.—*Estimated cost per ton of phosphoric acid (P_2O_5), 90 per cent yield, produced by smelting briquetted charges of mine-run phosphate in an oil-burning furnace.*

Items.	Cost.	Items.	Cost.
Briquetted material	$18.24	Labor of 18 men, at $5 per day	$3.00
Fuel oil, 360 gallons, at 2 cents per gallon	7.20	Insurance	.50
Power	3.50	Overhead expenses	1.50
Interest on $100,000, at 6 per cent	.55		
Depreciation on $100,000, at 20 per cent	1.82	Total cost per ton	36.31
		Total cost per unit	.36

TABLE 21.—*Estimated cost of producing 1 ton of available phosphoric acid (P_2O_5) in the form of double superphosphate by treating high-grade phosphate rock with phosphoric acid obtained by the fuel furnace process.*

Item.	Quantity.	Cost—	
		Per ton of material.	Per ton of product.
	Tons.		
Phosphate rock (washed)	0.98	$3.50	$3.43
P_2O_5 in form of 58° B. acid	[1] .67	36.31	24.35
Labor and power		[2] 1.30	2.68
Drying		[2] .25	.52
Total cost per ton P_2O_5			30.98
Total cost per unit P_2O_5			.31

[1] Equivalent to 1.08 tons of H_3PO_4 (58° B.).
[2] Cost per ton of material handled.

By comparing the figures given in Tables 20 and 21 with those in Tables 3 to 7, pages 15 and 16, it will be seen that the estimated cost per ton (or per unit) of P_2O_5 produced by the fuel furnace method is considerably below that obtained by either the electric furnace or sulphuric acid process. If the acid thus produced be used in the manufacture of double acid phosphate the economy of this method appears even more marked.

Whether or not efficiencies can be obtained throughout a protracted run commensurate with those indicated during certain short periods of actual operation must yet be proven, and it is the intention of the writers to establish this point, if possible, with the present plant by eliminating the mechanical difficulties already cited. But the fundamental principles established and the progress which has been made in large-scale experiments so far conducted make it appear that this general method of producing phosphoric acid will be commercially applied.

SUMMARY AND CONCLUSIONS.

During the last decade there has been a tendency toward a higher specialization in the American industries, but while the American fertilizer industry up to the time of the European war had shown a rather steady growth, in some regards it had lagged considerably behind. It is now apparent, however, that fertilizer practice as a whole and phosphate production in particular are on the verge of a profound change. This bulletin describes certain research investigations of the Fertilizer Division of the Bureau of Soils and was prepared with a view to showing the commercial possibilities of the volatilization process for producing phosphoric acid and phosphatic fertilizers.

The fundamental principles involved in the pyrolytic production of phosphoric acid are (1) at high temperatures, silica assumes the properties of a relatively strong acid and can displace the phosphoric acid of phosphate rock forming silicates of lime and free phosphoric anhydride (P_2O_5); (2) in the presence of a reducing agent, such as coke, elemental phosphorus is produced and the decomposition of the rock is brought about at considerably lower temperatures.

This process has four advantages over the sulphuric acid method of producing soluble phosphate. (1) Low-grade phosphates (high in silica) unfit for sulphuric acid treatment may be used, since the presence of silica is necessary for the smelting method. (2) Since the furnace process utilizes mine-run material, it is possible to dispense with the costly steps of washing and screening the rock, which entails the loss of so much phosphate. (3) The furnace process calls for no sulphuric acid, which under present conditions is hauled to the fertilizer plants as acid and hauled away again as gypsum in acid phosphate. This acid acts primarily as a reagent and actually dilutes the final product. (4) By the use of electric or fuel furnaces near the phosphate mines it is possible to produce a relatively concentrated product which can stand heavy handling charges and the cost of long freight hauls.

The pyrolytic process of producing phosphoric acid is based on the old method of making phosphorus, but the steps employed to-day are much less cumbersome and costly than in the earlier days of phosphorus manufacture. Numerous patents have been taken out

on methods of producing phosphorus, phosphoric acid, and phosphate compounds either in an electric or fuel furnace. In some of these processes a reducing agent is employed and in some the carbon is left out of the charge. Combinations of the fuel and electric furnaces have also been proposed, but until recently it has been the general belief that the complete volatilization of phosphoric acid from mixtures of phosphate rock, sand, and coke could only be attained in an electric furnace. Accordingly, the first work conducted in this bureau was carried on in a simple electric furnace using high-grade phosphate rock and fairly pure samples of sand and coke. In this investigation the Cottrell method of electrical precipitation was employed for the collection of phosphoric acid fumes. This method has proven very satisfactory and has the advantage of recovering the product in a relatively pure and concentrated form which can be handled and shipped at a minimum cost. A description of this precipitator equipment is given in detail.

The investigation was then carried out on a larger scale with a view to determining the commercial possibilities of the process. A cooperative arrangement was entered into with an outside concern and protracted tests made over a period of several days and weeks. Assuming power could be obtained at $25 per horsepower year the estimated cost per pound of P_2O_5 in the form of phosphoric acid was 3.37 cents, exclusive of interest, maintenance, and depreciation charges. No means of heat regeneration were employed, but even on the basis of these figures the cost of the unit of P_2O_5 was not very much in excess of that in acid phosphate during the war period, when the price of sulphuric acid was exceptionally high. Furthermore, by using the volatilized acid collected by the Cottrell precipitator for treating high-grade phosphate rock for the production of double superphosphate, the final cost of the unit of soluble P_2O_5 can be materially reduced. Since these experiments were conducted electric furnaces of commercial size for the simultaneous production of ferrophosphorus and phosphoric acid have been erected and economically operated. Most of the phosphoric acid produced, however, is sold for purposes other than fertilizers, as for these purposes it commands a higher price.

There is another factor, however, which has a direct bearing on the cost of manufacturing P_2O_5 by the furnace process. This is the great saving which can be effected by employing low-grade and run-of-mine phosphates unfit for treatment with sulphuric acid. A number of experiments were undertaken in the electric furnace at Arlington Experimental Farm, Va., to determine if these run-of-mine phosphates could be successfully employed in the volatilization process. The results of this investigation are given in tabulated form, showing that complete volatilization of phosphoric acid may be readily obtained by the use of such charges. There are given also the estimated costs of phosphoric acid per ton and per unit by the sulphuric acid process and by the electric furnace process, using in some cases high-grade washed rock, and in others run-of-mine phosphates, and then treating phosphate rock with the phosphoric acid thus obtained. These estimates show that by the use of run-of-mine phosphates it is possible to reduce the cost per unit of P_2O_5 to a point where it compares more favorably with that produced by the sulphuric acid

method. The main cost in producing phosphoric acid in the electric furnace is that of electric power, but with a properly designed furnace and efficient auxiliary equipment it should be possible to reduce the power cost per unit of phosphoric acid very materially. Tables are given containing the thermal heat balance of two types of electric furnaces, one in which practically all of the heat in the effluent gases is lost and the other of the shaft type wherein much of the heat is regenerated. It is pointed out that in a furnace charge containing sufficient carbon for the reduction of the phosphoric acid to elemental phosphorus the over-all furnace reactions are exothermic. If, therefore, no heat were lost in the evolved gases from radiation and in the slag which is tapped off the reactions when started should go to an end without power consumption.

While it is entirely possible that future developments of our water-power resources may make electric energy available at a price considerably below the present prevailing rates, under existing conditions the thermal unit can be obtained very much more cheaply from burning fuel than it can by electric energy. Therefore, if the necessary temperature can be attained and the conditions fulfilled for volatilizing phosphoric acid by means of burning fuel in lieu of the electric arc a great saving in the cost of production should be effected. Charts and a table comparing the cost of the heat unit produced by electric power at present rates with that obtained from standard fuels at prevailing prices show very conclusively that the cost of the thermal unit obtained by fuel is far below that obtained by electric energy.

The writers therefore undertook an investigation to determine if fuel could not be substituted for the electric arc. In the preliminary laboratory experiments where pure samples of tricalcium phosphate, quartz flour, and coke were employed it was found possible to completely eliminate phosphoric acid from such mixtures providing reducing conditions were maintained within the mass and the materials so proportioned as to give a rather highly siliceous but fusible slag. The ratio of silica to lime adopted was approximately 61 to 39, which is very close to the proportions of these ingredients in calcium trisilicate ($Ca_2Si_3O_8$). The work was then continued on a larger scale. In these tests mine-run phosphates were employed and an oil-burning furnace used of such a design that the charge was heated indirectly. This type of furnace was abandoned as impractical since it was evident that in order to make the process economically practical the full calorific power of the fuel should be utilized, which can only be done by the direct heating of the mass. The most practical type of furnace to employ seemed to be a modified form of the blast furnace, but in order to maintain reducing conditions and handle a charge of mine-run phosphate containing much finely divided material it was necessary to briquet or nodulize the mixture. Accordingly, experiments were undertaken with a view to briquetting the mixtures of finely ground phosphate, sand, and coke. Various binders were employed, but none of them were satisfactory either from the standpoint of price or their poor binding qualities. It was found, however, that in many typical phosphate deposits the percentage of very finely divided material which is classed as clay was ample to give the mixture sufficient plasticity to make excellent briquets when the mass was moistened with about 7 to 10 per cent water. Many

deposits of run-of-mine phosphate in Florida and Tennessee are of such composition that they can be used in the furnace process either by the addition of sand to raise their silica content or by reinforcing with somewhat high-grade phosphates to give the proper silica-lime ratio in the charge. A series of laboratory tests were conducted with a view to determining the best proportions of silica and lime in the briquetted charge for the most rapid evolution of P_2O_5. The nearly complete volatilization of phosphoric acid from briquets having a silica-lime ratio of 69 to 31 was attained in from 30 to 35 minutes and the slag was sufficiently molten to flow freely at 1,600° C. Another point brought out by these experiments was the possibility of using bituminous coal as a reducing agent in the briquets in lieu of coke.

The large scale operations on smelting briquetted charges of phosphate rock, sand, and coke were practically all conducted in a furnace holding 700 pounds of briquetted charge and having certain features of both the open-hearth and blast-furnace types. Near the top of the furnace shaft a flue leads into a dust chamber and from thence into a series of stoves for burning any combustible gases evolved from the furnace and regenerating the heat in the effluent gases. The auxiliary equipment of this earlier furnace was not entirely satisfactory, so it was later torn down and replaced by more suitable equipment. Oil burners set into water-cooled steel jackets furnished the fuel required for the heating of the furnace and in the earlier work three small positive-pressure blowers delivered the air required for the combustion of this oil. The phosphate used in these experiments was mine-run material obtained from the hard-rock fields of Florida. Two tests conducted with this equipment are recorded, one of these lasting for a period of only 10 hours and the other for a period of 20 hours. In the first experiment an average evolution of 52 per cent of P_2O_5 was obtained from the charge, and while the slag finally congealed to the point where it was not possible to tap the furnace, the fuel consumption toward the latter part of the run indicated that the rate of evolution was 88.5 pounds per hour or 8½ pounds of P_2O_5 per gallon of fuel oil consumed.

The next test was continued for a period of 20 hours, during which time 3,500 pounds of briquetted charge were smelted and run out of the furnace as a molten slag. While numerous mechanical difficulties were encountered in the earlier stages of this run, during the last 3½ hours the furnace operated quite efficiently, temperatures as high as 1,600° C. being attained during this period and an average volatization of 97 per cent P_2O_5 obtained. The rate of evolution during the latter part of this test was 46.3 pounds of P_2O_5 per hour with a fuel-oil consumption of 8.3 gallons per hour. On this basis a volatilization of 5½ pounds of P_2O_5 per gallon of fuel oil was obtained. While the electrical precipitator was operated for only a portion of the time, a considerable quantity of phosphoric acid varying in strength from 21.5 to 64 per cent H_3PO_4 was collected, the stronger acid being obtained toward the last of the test when the temperature of the system had risen to the point where very much less moisture was condensed.

The refractory lining of the furnace after this test, however, was found to be in such bad condition that the furnace proper was rebuilt and carborundum brick used in those portions where the highest

temperature is attained. A new blower was installed, better auxiliary equipment for conserving the heat of the evolved gases built, and a recording pressure gauge and pyrometers also installed. The furnace proper of this plant was operated a number of times, but it was finally decided to water-cool the furnace in order to conduct tests over more protracted periods. Accordingly a new furnace shaft consisting of a steel shell lined with carborundum and fire brick was constructed, over which a water curtain was caused to flow. Later a gas-tight steel shell (water-cooled) was also built around the furnace crucible and cast-iron cinder notches (water-cooled) inserted in the slag holes. One of the tests conducted with the new equipment was continued efficiently for five and a half hours after the furnace was first charged, and during this period 1,175 pounds of briquets were smelted and tapped off as a molten slag. The phosphoric acid content of this slag was 0.72 per cent, equivalent to a volatilization of 96.7 per cent of P_2O_5, but since the fuel-oil consumption was relatively high (17 gallons per hour) the yield of P_2O_5 per gallon of fuel oil was only 3.2 pounds. Just after the furnace was tapped an explosion blew off the top of one of the stoves and rendered a continuation of this test impracticable.

The next test was continued for a period of 70 hours, during which time over 4 tons of charge were smelted and tapped off as a molten slag. The data obtained during this 3-day run was not altogether satisfactory, owing to a number of mechanical difficulties and the poor quality of the fuel oil used. A volatilization of from 46 to 94.5 per cent of P_2O_5 was obtained, but the sediment in the crude oil necessitated a very much higher fuel consumption than was desirable for the efficient working of the furnace. Therefore the relation between the P_2O_5 evolved and the fuel consumed was very unfavorable. This last furnace equipment, however, stood up admirably under the high temperatures attained and is in a stand-by condition for further experimentation.

The results of the tests so far conducted with the semicommercial equipment at Arlington Experimental Farm, Va., have demonstrated conclusively that it is feasible to drive off phosphoric acid practically completely from run-of-mine phosphates in large-scale operations by means of burning fuel. They have also shown that a furnace can be constructed which will withstand for a protracted period the combined effects of extremely siliceous slags and the high temperatures attained in this process, but before data can be obtained which will show conclusively the commercial feasibility of producing phosphoric acid by this process a number of the mechanical difficulties encountered must be remedied.

During the tests so far conducted, however, with the semicommercial equipment, there were periods of from three to five hours when the furnace appeared to operate quite efficiently, and if the data taken at such times are considered indicative of normal working conditions, the volatilization method of producing phosphoric acid appears economically superior to the ordinary sulphuric acid method or to the electric-furnace process. Based on the data gathered between certain periods of actual operation the estimated cost of production by the fuel-furnace process is $36.31 per ton (or 36 cents per unit) of P_2O_5 in the form of 75 per cent H_3PO_4 and $30.98 per

ton (or 31 cents per unit) of P_2O_5 in the form of double acid phosphate. These figures are from $8 to $13 below the most favorable ones recorded for the production of a ton of P_2O_5 by the electric-furnace and sulphuric acid methods. Whether or not efficiencies can be obtained through a more extended run commensurate with those indicated during these short periods must yet be proven, but certain fundamental principles have been established, and such progress has been made that it appears likely this general method of producing phosphoric acid will be commercially applied.

ORGANIZATION OF THE UNITED STATES DEPARTMENT OF AGRICULTURE.

November 26, 1923.

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